Issued July 20, 1911.

U. S. DEPARTMENT OF AGRICULTURE.
BUREAU OF CHEMISTRY—BULLETIN No. 137.
H. W. WILEY, Chief of Bureau.

PROCEEDINGS

OF THE

TWENTY-SEVENTH ANNUAL CONVENTION

OF THE

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS,

HELD AT

WASHINGTON, D. C., NOVEMBER 10-12, 1910.

EDITED BY
HARVEY W. WILEY,
SECRETARY OF THE ASSOCIATION.

WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1911.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Chemistry,
Washington, D. C., January 10, 1911.

Sir: I have the honor to submit for your approval the Proceedings of the Twenty-seventh Annual Convention of the Association of Official Agricultural Chemists. The reports herein submitted are of fundamental importance in evolving accurate and uniform methods of analysis for the materials discussed, these methods being of increasing importance in the administration of the various laws, State and National, regulating traffic in foods, drugs, fertilizers, insecticides, etc. The material has been carefully condensed as far as the detailed nature of the work will permit, and I recommend the publication of the report as Bulletin 137 of the Bureau of Chemistry.

Respectfully,

H. W. Wiley,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

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FIRST DAY.

THURSDAY—MORNING SESSION.

By vote of the executive committee, Washington, D. C., was chosen as the meeting place of the twenty-seventh annual convention of the Association of Official Agricultural Chemists. The convention was called to order on the morning of November 10 at the Raleigh Hotel, with Mr. W. A. Withers, of Raleigh, N. C., the president, in the chair. The following members and visitors were present:

MEMBERS AND VISITORS PRESENT.

Adams, A. B., Bureau of Internal Revenue, Treasury Department, Washington, D. C.
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No report was presented on phosphoric acid nor on the availability of phosphoric acid in basic slag. By vote of the association the following paper on the subject by Mr. Whitehouse was heard by the association and referred to the appropriate committee on recommendations for consideration. The paper was as follows:

WAGNER METHOD FOR DETERMINATION OF SOLUBLE PHOSPHORIC ACID IN BASIC SLAGS.

By W. L. Whitehouse.

The question of adopting a method for the determination of soluble phosphoric acid in basic slags has been brought before this association on several occasions. Up to the present time, however, there has been no method adopted which agrees consistently with the actual effectiveness of this material as shown by pot experiments in the hands of experimenters or by the practical growing of crops.

This has been due no doubt to the fact that basic slag had not come into general use and consequently very few experiment stations were called upon to value this class of material. At the present time, however, large quantities of Thomas phosphate powder are being imported and offered for sale on our markets and manufacturers of this material state that the shipment of still larger amounts is contemplated. In view of these facts it is unfortunate that we are somewhat unprepared to give the consumer the protection due him and at the same time do justice to the conscientious manufacturer. Furthermore, as nearly all States require a guarantee of available phosphoric acid in fertilizers offered for sale, in the case of basic slag it is quite impossible to comply with these laws owing to the absence of any definite method by which this material may be officially valued.

The regular official method used for determining the solubility of phosphoric acid in fertilizers is obviously unsuitable and misleading when applied to such material as Thomas phosphate powder. This fact was early recognized, but few attempts were made to use this method for valuing this material.

At the annual meeting of this association in 1907 it was proposed to adopt the method now known as the "fineness" method. This, while not entirely without merit, has a tendency to work against the consumer as well as the manufacturer of a really high-grade slag, giving the unscrupulous dealer the advantage by furnishing the means of adulteration and fraud. Wagner and others have repeatedly called attention to the fact that slags of like phosphoric acid content, which are richest in silicic acid, give the best results when tested by pot experiments. This is claimed to be probably due to the fact that the phosphoric acid in slags of this character exists as a double salt of tri-calcic phosphate and calcium silicate, which compound is readily available to the growing plant. However this may be, it has been shown that the composition of different slags varies widely and that their effectiveness depends in a large measure upon their composition.

By means of pot experiments, as well as by laboratory investigations, Wagner has shown that the phosphoric acid in slags of the same degree of fineness varies in availability from 30 to 90 per cent. The relationship, therefore, between the composition and the effectiveness of basic slags is not taken into consideration when they are valued according to their fineness and their total phosphoric acid content. It therefore becomes evident that a method to be just and equitable must be one in which the reactions will be in harmony with the physical and chemical composition of the slag.

Of the methods thus far considered and experimented with that of Wagner seems to have the most merit. As we can not, of course, hope to duplicate exactly the reactions of soil and plant constituents in their natural state, the most that can be expected

of any method is to approximate this to a reasonable degree, limited by the nature of the case.

The Wagner method has for its object the solution of the easily decomposable compounds of phosphoric acid in a 2 per cent solution of citric acid at a temperature of 17.5° C. By means of this method Wagner has shown that with 28 samples of slags of different makes and compositions, the average solubility of the phosphoric acid content was 89 per cent while the actual effectiveness as shown by pot experiments was 88 per cent. As some of these slags were found to be adulterated with insoluble mineral phosphate, the merits of this method are obvious.

The writer has examined many samples of slag which according to the fineness method indicated a high degree of availablity, but which showed a comparatively low degree of availability when tested by the Wagner method. Some of these samples were found to be contaminated with insoluble mineral phosphates, while in others their inferiority was probably due to their composition. All the data which have been accumulated by European experimenters indicate that the Wagner method has great merit, and in recognition of this the method was adopted by the Union of German Experiment Stations in 1906.

Ignoring the fact of the comparative agricultural value of slags as far as other forms of phosphatic materials are concerned, it ought not to be overlooked that this material is offered for sale in large quantities on our markets. At the present time and with our present methods we are unable to discriminate between a good slag and a bad slag, and the most important issue concerns the adoption of a method which will enable us to do this. From the standpoint of the German experiment stations, in a country where many thousands of tons of basic slag are used annually, the method of Wagner has proved eminently satisfactory to all concerned, and in the light of their experience, which covers a period of 20 years, it is conceivable that the adoption of this method in this country, at least provisionally, would be a decided advantage.

We need not depend entirely upon the results obtained by European experimenters, however, for we have plenty of data furnished by some of the leading experimenters in this country which substantiate the fact beyond the shadow of a doubt that the phosphoric acid in basic slag is fully as available to the growing plant as that in the soluble forms. Experiments conducted at the Rhode Island station, reported in their Bulletin 114, show that the average increase in yield of nine different crops on limed soil, due to the phosphoric acid applied, was 34 per cent with dissolved bone black, 35 per cent with acid phosphate, and 37 per cent with basic slag. These figures indicate that basic slag is equal in effectiveness to the soluble forms used. This being shown by actual plat tests, it is logical to believe that the laboratory test of their solubility should show the same degree of uniformity. By the official method, using the neutral ammonium citrate solution, the soluble forms show an average solubility of 90 per cent while the Wagner method shows the average solubility of the phosphoric acid in basic slag to be 89 per cent. These solubility figures are in perfect harmony with the actual effectiveness of these materials as shown by the work of the Rhode Island station.

Experiments conducted at the Ohio station, reported in their Circular 93, show that with three different crops on limed soil the average increase in yield due to the phosphoric acid applied was 55 per cent with acid phosphate, 51 per cent with dissolved bone black, and 46 per cent with basic slag. These figures, while they are somewhat higher than those of the Rhode Island station, also tend to confirm the uniformity in effectiveness of the phosphoric acid in the three forms.

The Maryland station in their Bulletin 114 show that the average increase in yield of wheat due to phosphoric acid was 82 per cent with double superphosphate, 82 per cent with dissolved bone black, 73 per cent with basic slag, and 49 per cent with acid phosphate. Experiments conducted at the Massachusetts station show that the

phosphoric acid in basic slag ranks as high in effectiveness as that in the soluble forms.

All of these investigations tend to confirm the results of Wagner, and furnish sufficient justification for the adoption of his method. It is hoped, therefore, that this method will be provisionally adopted at this meeting, and that further investigations by the committee will be made during the ensuing year, so that the association may satisfy itself that the method has sufficient merit to warrant its permanent adoption.

REPORT ON NITROGEN.

By C. H. Jones, *Referee.*

No cooperative work on nitrogen has been done during the past year. The referee desires again to call the attention of the association to the important question of the availability of organic nitrogen in fertilizers and crude stock. This subject is now being investigated by a committee appointed last March by the directors of the several New England, New York, and New Jersey stations. A prominent fertilizer company has afforded this committee abundant opportunity to look into the manufacture of commercial goods as now conducted and to secure a number of authentic samples of base goods (by the wet-mixing process) and crude nitrogen stock.

Two provisional methods for the laboratory determination of organic nitrogen availability appear in the methods of this association (Bulletin 107, revised, pages 10 to 11), namely, the neutral permanganate and the alkaline permanganate methods. Within the past year and a half, these methods have been slightly modified by their originators with the view to adapting them more perfectly to the purpose for which they were intended. Street has modified the neutral permanganate method by recommending that an equivalent of 45 mg of water-insoluble organic nitrogen be employed for the determination. The filter paper is also eliminated during the permanganate digestion which necessitates a few minor changes in manipulation.

The alkaline permanganate method has been modified by the writer, who recommends that an amount of material equivalent to 50 mg of organic nitrogen or water-insoluble organic nitrogen be used. The strength of the permanganate solution is also increased, it now being on a basis of 2.5 per cent potassium permanganate instead of 1.6 per cent as formerly. The methods as restated to include these modifications read as follows:

Laboratory Methods for Organic Nitrogen Availability.

modified alkaline permanganate method.

Total organic nitrogen basis.—Weigh an amount of material equivalent to 50 mg of organic nitrogen into a 600 cc Kjeldahl distillation flask. Add 20 cc of water and 100 cc of alkaline permanganate solution (25 grams of pure potassium permanganate and 150 grams of sodium hydroxid separately dissolved in water, the solutions cooled, mixed, and made to bulk of one liter). Connect with an upright condenser to which a receiver containing standard acid has been attached. Digest slowly (below distillation point) for 30 minutes. Gradually increase the temperature and boil until 95 cc of distillate is obtained; titrate as usual. Make a correction for any ammonia contained in the sample. During the digestion an occasional gentle rotation is desirable, and if the material shows a tendency to adhere to the sides of the flask during the distillation, the same procedure is advised. The per cent of nitrogen obtained on the above 5 per cent basis multiplied by 20 equals per cent availability.

Water-insoluble nitrogen basis.—Weigh an amount of material equivalent to 50 mg of water-insoluble organic nitrogen [1] onto a filter. Wash with successive portions of water until the filtrate amounts to about 250 cc. Dry the residue at a temperature not exceeding 80° C. and transfer same from the filter into a 600 cc Kjeldahl distilla-

[1] Determine by washing 1 gram of the material on an 11 cm filter with water at room temperature, to a volume of about 250 cc. Dry and determine nitrogen in the residue, making a correction for the nitrogen in the filter paper if necessary.

tion flask. Add 20 cc of water and 100 cc of alkaline permanganate solution and proceed as under total organic nitrogen basis. No correction is necessary for ammonia.

NEUTRAL PERMANGANATE METHOD.

Weigh a quantity of the fertilizer, equivalent to 45 mg of water-insoluble organic nitrogen,[1] on a moistened 11 cm filter paper, and wash with successive portions of water at room temperature until the filtrate amounts to 250 cc. Transfer insoluble residue with 25 cc of tepid water to a 300 cc low-form Griffin beaker, and add 100 cc of a 2 per cent permanganate solution. Digest in a steam or hot water bath for 30 minutes at the temperature of boiling water, covering the beaker with a watch glass and setting well down into the bath so that the level of the liquid in the beaker is below that of the bath. Stir twice at intervals of 10 minutes. At the end of the digestion remove from the bath, add 100 cc of cold water, and filter through a heavy 15 cm folded filter. Wash with cold water, small quantities at a time, until total filtrate amounts to about 400 cc. Determine nitrogen in residue and filter, correcting for the nitrogen of the filter.

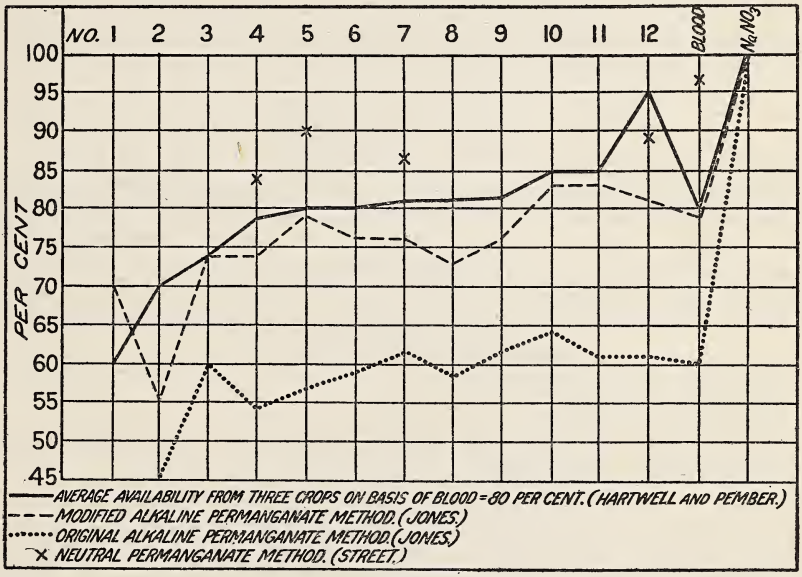

FIG. 1.—Nitrogen availability of samples representing the water-insoluble portion of commercial fertilizers. (Results from pot experiments compared with figures by the modified alkaline permanganate method on similar samples.)

B. L. Hartwell and F. R. Pember are now conducting a series of pot experiments, using as the nitrogen source the authentic samples previously mentioned, together with the water-insoluble residues from officially collected commercial fertilizers. When sufficient actual crop performance data have been obtained, the results can be compared with the availability figures already secured on similar samples by the laboratory methods outlined.

Through the courtesy of Mr. Hartwell the writer was recently furnished with small portions of a series of samples representing the water-insoluble portion of several commercial fertilizers. These samples had furnished the nitrogen for a three-crop pot experiment, conducted at the Rhode Island station, and a summary of the crop data on a basis of dried blood 80 per cent available, together with the results obtained by the writer with the modified and the original alkaline permanganate methods, is outlined on the accompanying chart (fig. 1). Mr. Street has as yet tested only four of these samples, and his findings are indicated on the chart by a cross (x). The

[1] See footnote on page 14.

agreement of the laboratory tests with the data afforded by these pot experiments is very marked and it is hoped that future results will be equally satisfactory. This subject of availability of nitrogen is brought before you at this time simply as a suggestion for future work by your next referee on nitrogen.

The report of the referee on separation of meat proteids, Mr. Moulton, was, in his absence, presented by Mr. Trowbridge. This paper will be found on page 148, in connection with the report on vegetable proteids.

President Withers appointed the following committee to wait upon the Secretary and the Assistant Secretary of Agriculture and invite them to address the association: R. Harcourt, Canada; R. J. Davidson, Virginia; and M. E. Jaffa, California. The following members of the committee on resolutions were also named: B. B. Ross, Alabama; A. L. Winton, Illinois; and W. H. McIntire, Pennsylvania.

REPORT ON POTASH.

By E. L. Baker, *Referee.*

The potash work has been very similar to that of last year, being a continuation of the study of Drushel's volumetric cobalti-nitrite method in comparison with the official method. In addition a gravimetric method, using the cobalti-nitrite reagent as a precipitant, and a test of a modification of the official method of making up the potash solution, as described by Breckenridge,[1] have been included in the work.

Three samples with the following directions were sent to cooperating chemists:

Association Potash Work, 1910.

Sample No. 1.—Commercial muriate.
Sample No. 2.—Kainite.
Sample No. 3.—A complete mixed fertilizer.
Potash to be determined by the official, the volumetric cobalti-nitrite, and the gravimetric cobalti-nitrite methods.

DRUSHEL'S VOLUMETRIC METHOD,[2] SLIGHTLY MODIFIED.

Dissolve 220 grams of sodium nitrite in 400 cc of water, 113 grams of cobalt acetate in 300 cc of water, and add 100 cc of glacial acetic acid to the latter. Mix the two solutions and warm gently.[3] Nitrogen tetroxid (NO_2) is evolved and the solution becomes dark colored. Remove the nitrogen tetroxid by means of a water pump kept running overnight. A yellow precipitate settles. Filter the solution and dilute with water to a liter.

Standard solutions.—Tenth-normal potassium permanganate and a tenth-normal oxalic-acid solution containing 50 cc of concentrated sulphuric acid per liter.

Solutions of fertilizer to be made up according to the official method.

Sample No. 1.—Run 5 cc of the solution, equal to 0.1 gram, from a burette into a porcelain evaporating dish, dilute with about 20 cc of water, add 1 cc of glacial acetic acid and 10 cc of sodium cobalti-nitrite reagent. Evaporate to a thick sirup over a steam bath (do not evaporate to dryness), cool, stir with cold distilled water until excess of sodium cobalti-nitrite reagent has dissolved; allow to settle and decant two or three times through a small funnel fitted with a perforated plate and a thick pad of ignited asbestos, or if preferred a Gooch crucible may be used. Transfer the precipitate to the filter and wash thoroughly with water. Blow the precipitate and asbestos into a 300 cc beaker; dilute with distilled water, add an excess of tenth-normal potassium permanganate (about 65 cc), stir and bring to boiling.[4] As soon as a dark-colored precipitate forms, add 5 cc of 1:1 sulphuric acid, stir well, and add an excess of tenth-normal

[1] J. Ind. Eng. Chem. 1909, 1 (7): 409; 1909, 1 (12): 804.
[2] Chem. News, 1908, 97: 124.
[3] Adie and Wood, Jour. Chem. Soc. 1900, 77: 1076.
[4] Bowser, J. Ind. Eng. Chem. 1909, 1 (12): 791.

oxalic acid (15 cc). Keep the solution hot until it becomes clear and the precipitate is completely dissolved, then titrate to color with tenth-normal potassium permanganate. From the whole amount of permanganate employed subtract the permanganate equivalent of the oxalic acid used and multiply the remainder by the factor 0.000856, which is the factor for strictly tenth-normal permanganate.

GRAVIMETRIC COBALTI-NITRITE METHOD.

Precipitate precisely as above. Filter through a Gooch crucible, wash thoroughly with water and finally four or five times with 80 per cent alcohol. Dry at least one hour at 100° C. and weigh. Multiply by the factor 0.2075.

Sample No. 2.—Pipette 25 cc of the solution, equivalent to 0.5 gram, into a porcelain evaporating dish, add 1 cc of glacial acetic acid and 10 cc of sodium cobalti-nitrite reagent and determine potash by the volumetric and gravimetric cobalti-nitrite methods as in sample No. 1, using about 80 cc of potassium permanganate.

Sample No. 3.—(a) Pipette 50 cc of the solution into a platinum evaporating dish, evaporate, add 1:1 sulphuric acid, and ignite as in the official method. Transfer to a porcelain evaporating dish with hot water and concentrate to a volume of about 25 cc, add 1 cc of glacial acetic acid and 10 cc of reagent. Proceed as in sample No. 1, using about 60 cc of permanganate and 15 cc of oxalic acid.

(b) In sample No. 3 also determine potash as follows: Weigh 5 grams upon a 12.5 cm filter paper and wash with successive small portions of hot water into a 500 cc flask to a volume of about 400 cc. Add 5 cc of concentrated hydrochloric acid, heat to boiling, and precipitate with ammonium hydroxid and ammonium oxalate in the usual way. Finish by the official method.

In making up the solution of sample No. 3 care should be taken to filter at once, after precipitating with ammonium hydroxid and ammonium oxalate and cooling, as long standing of the solution in the presence of the insoluble matter seems to produce higher results in potash. Corrections should be made for blanks upon all determinations.

Analytical Results.

Comparative results of official, volumetric and gravimetric cobalti-nitrite methods for potash determinations.

Chemist.	Sample No. 1.			Sample No. 2.			Sample No. 3.			
	Official method.	Volumetric cobalti-nitrite method.	Gravimetric cobalti-nitrite method.	Official method.	Volumetric cobalti-nitrite method.	Gravimetric cobalti-nitrite method.	Official method.	Volumetric cobalti-nitrite method.	Gravimetric cobalti-nitrite method.	Modified official method.
B. E. Curry, Durham, N. H.	.....	50.03	50.46	12.44	12.11	12.43	4.60	4.54	5.37	4.72
	50.70	49.99	50.63	12.46	12.16	12.45	4.68	4.41	5.37	4.74
	50.70	50.32	50.75	.....	12.19	12.57	.....	4.47	.....	4.68
Average	50.70	50.11	50.61	12.45	12.16	12.48	4.64	4.48	5.37	4.71
P. L. McCreary and P. L. Hibbard, Berkeley, Cal.	51.64	47.76	51.20	12.73	12.20	12.65	4.68	4.17	5.27	4.83
	51.64	46.73	51.18	12.72	12.17	13.22	4.68	4.00	4.65	4.84
	51.72	47.17	.....	.....	12.27	11.90	.....	.....	.....	.....
	.....	.....	.....	.....	.....	11.97	.....	4.05	.....	.....
Average	51.68	47.22	51.19	12.73	12.21	12.44	4.68	4.07	4.96	4.84
Cornelius Beatty, College Park, Md.	53.24	51.43	52.21	12.61	12.55	12.80	4.92	4.42	5.10	5.04
	53.26	51.43	52.23	12.69	12.57	12.81	4.94	4.47	5.11	5.10
	.....	51.43	.....	12.70	12.70	12.85	4.89	4.52	5.25	.....
	.....	.....	.....	.....	12.79	12.86	.....	4.58	.....	.....
	.....	.....	.....	.....	.....	13.04	.....	4.60	.....	.....
	.....	.....	.....	.....	.....	.....	.....	4.65	.....	.....
Average	[1] 53.25	51.43	52.22	12.67	12.65	12.87	[1] 4.92	4.54	5.15	[1] 5.07
W. W. Murray, Baltimore, Md., average	52.12	51.53	52.49	12.60	12.18	12.41	4.63	4.54	4.94	4.70

[1] Omitted from general average.

Comparative results of official, volumetric and gravimetric cobalti-nitrite methods for potash determinations—Continued.

Chemist.	Sample No. 1.			Sample No. 2.			Sample No. 3.			
	Official method.	Volumetric cobalti-nitrite method.	Gravimetric cobalti-nitrite method.	Official method.	Volumetric cobalti-nitrite method.	Gravimetric cobalti-nitrite method.	Official method.	Volumetric cobalti-nitrite method.	Gravimetric cobalti-nitrite method.	Modified official method.
I. R. Rothrock and A. C. Johnson, Baltimore, Md., average.	51.71	51.75	51.80	12.51	12.54	12.55	4.74	.....	.....	4.66
O. M. Shedd, Lexington, Ky.	52.05	51.87	.....	12.76	12.60	.....	4.66	4.68	.....	.....
	51.96	52.26	.....	12.87	12.69	.....	4.66	4.63	.....	.....
	.....	51.79	.....	.....	12.57	.....	.....	.....	.....	.....
	.....	51.45	.....	.....	12.54	.....	.....	.....	.....	.....
	.....	51.45	.....	.....	.....	.....	.....	.....	.....	.....
	.....	51.36	.....	.....	.....	.....	.....	.....	.....	.....
	.....	51.04	.....	.....	.....	.....	.....	.....	.....	.....
	.....	51.59	.....	.....	.....	.....	.....	.....	.....	.....
Average	52.01	51.60	.....	12.82	12.60	.....	4.66	4.66	.....	.....
R. C. Wiley, Manhattan, Kans.	51.88	46.10	46.11	12.79	11.43	11.78	4.98	4.65	6.61	4.84
	51.98	47.97	48.16	12.90	10.27	12.09	4.89	4.72	6.90	4.86
	51.88	48.60	.....	12.82	.....	.....	4.87	.....	5.42	.....
	51.98	.....	.....	12.77	.....	.....	4.82	.....	.....	.....
	52.17	.....	.....	.....	.....	.....	.....	.....	.....	.....
	52.07	.....	.....	.....	.....	.....	.....	.....	.....	.....
Average	51.99	[1]47.56	47.14	12.82	[1]10.85	11.94	4.39	4.69	6.31	4.85
L. F. Whipple, Kingston, R. I.	51.05	50.89	51.99	12.60	13.04	12.96	4.76	4.55	6.80	.....
	51.04	50.82	51.97	12.59	12.97	12.94	4.75	4.48	6.78	.....
Average	51.05	50.86	51.98	12.60	13.01	12.95	4.76	4.52	6.79	.....
R. M. Pinckney, Bozeman, Mont.	51.96	51.53	52.92	13.18	12.56	13.62	4.59	4.72	6.89	.....
	52.08	51.61	54.26	13.06	12.20	13.96	4.53	4.47	6.18	.....
	.....	51.45	54.99	.....	12.51	13.13	.....	4.34	6.42	.....
	.....	53.95	55.61	.....	12.60	13.21	.....	4.22	6.44	.....
	.....	51.29	54.16	.....	12.62	.....	.....	4.54	.....	.....
	.....	49.55	55.01	.....	12.37	.....	.....	4.29	.....	.....
	.....	.....	53.49	.....	12.14	.....	.....	4.64	.....	.....
	.....	.....	.....	.....	12.27	.....	.....	2.24	.....	.....
	.....	.....	.....	.....	.....	.....	.....	4.60	.....	.....
	.....	.....	.....	.....	.....	.....	.....	4.26	.....	.....
Average	52.02	51.56	54.35	13.12	12.41	13.23	4.56	4.43	6.48	.....
E. L. Baker, Geneva, N. Y.	51.92	52.04	51.09	12.85	12.93	12.72	4.63	4.61	4.86	4.82
	52.00	52.13	51.58	12.86	12.93	12.89	4.61	4.69	4.84	4.79
	.....	.....	50.88	.....	.....	.....	.....	.....	4.84	.....
	.....	.....	.....	.....	.....	.....	.....	.....	4.79	.....
Average	51.96	52.09	51.18	12.86	12.93	12.81	4.62	4.65	4.83	4.81
William Rodes, Lexington, Ky.	52.03	.....	.....	12.74	.....	.....	4.70	.....	.....	4.81
	51.97	.....	.....	12.69	.....	.....	4.73	.....	.....	4.70
	.....	.....	.....	.....	.....	.....	.....	.....	.....	4.87
	.....	.....	.....	.....	.....	.....	.....	.....	.....	5.04
Average	52.00	.....	.....	12.72	.....	.....	4.72	.....	.....	4.86
Otto McCreary, Geneva, N. Y.	51.98	51.51	52.50	12.80	12.82	13.09	4.64	4.69	4.63	4.82
	52.00	52.61	53.88	12.72	12.70	12.77	4.65	4.73	4.68	4.90
	.....	54.00	53.22	.....	12.77	12.93	.....	.....	.....	4.86
	.....	53.92	54.59	.....	.....	12.95	.....	.....	.....	.....
	.....	.....	54.34	.....	.....	13.01	.....	.....	.....	.....
	.....	.....	54.28	.....	.....	.....	.....	.....	.....	.....
	.....	.....	53.76	.....	.....	.....	.....	.....	.....	.....
Average	51.99	53.01	53.89	12.76	12.76	12.95	4.65	4.71	4.66	4.86

[1] Omitted from general average.

Comparative results of official, volumetric and gravimetric cobalti-nitrite methods for potash determinations—Continued.

Chemist.	Sample No. 1.			Sample No. 2.			Sample No. 3.			
	Official method.	Volumetric cobalti-nitrite method.	Gravimetric cobalti-nitrite method.	Official method.	Volumetric cobalti-nitrite method.	Gravimetric cobalti-nitrite method.	Official method.	Volumetric cobalti-nitrite method.	Gravimetric cobalti-nitrite method.	Modified official method.
H. H. Hill, Blacksburg, Va....	51.93	51.67	51.99	12.90	12.98	13.08	4.66	4.43	4.56	4.78
	51.99	51.85	51.96	13.09	13.01	13.13	4.71	4.52	4.58	4.81
	51.89	51.81	51.93	.....	12.84	.....	4.70	4.56	4.55	.....
	51.92	51.86	51.96	.....	12.51	.....	4.61	.....	.....	.....
	51.93	51.83	51.92	.....	.....	.....	.....	.....	.....	.....
Average.....	51.93	51.80	51.95	13.00	12.84	13.11	4.67	4.50	4.56	4.80
M. P. Sweeney, Geneva, N. Y.	51.80	51.50	51.90	12.66	12.95	12.89	4.69	4.61	4.63	4.87
	51.97	51.33	52.00	12.59	12.87	12.97	4.70	4.63	4.69	4.91
	.....	.....	.....	.....	12.97	.....	.....	.....	.....	.....
	.....	.....	.....	.....	13.07	.....	.....	.....	.....	.....
Average.....	51.89	51.42	51.95	12.63	12.97	12.93	4.70	4.62	4.66	4.89
C. C. Hedges and.....(H)	52.09	51.04	51.83	12.96	12.54	12.90	4.65	4.38	4.71	4.83
R. E. Rice, Ithaca, N. Y. (R)	51.95	.....	52.15	12.70	11.84	12.81	4.65	.....	4.81	4.73
Average[1].....	52.02	51.04	51.99	12.83	12.54	12.86	4.65	4.38	4.76	4.78
J. C. Jurrjens, Madison, Wis...	50.62	50.25	50.42	12.16	12.29	12.46	4.82	4.84	7.49	5.29
	51.04	50.16	50.35	12.30	12.28	12.56	4.88	4.73	7.94	5.11
	50.86	49.64	50.48	12.36	12.36	12.81	4.62	4.51	7.84	5.44
	50.90	.....	.....	.....	.....	.....	.....	4.69	7.84	5.28
Average[1].....	50.85	50.01	50.41	12.27	12.31	12.61	4.77	4.69	7.77	5.28
L. E. Morgan,[2] Columbia, Mo..	52.30	54.32	55.22	13.68	13.11	13.11	4.99	4.90	5.73	.....
	52.39	53.55	54.92	13.88	13.35	13.20	4.96	4.91	5.19	.....
	54.32	53.46	54.41	.....	13.15	13.23	.....	4.78	5.21	.....
Average[1].....	52.34	53.78	54.85	13.73	13.20	13.18	4.98	4.86	5.38	.....
General average.....	51.77	50.92	51.72	12.73	12.61	12.72	4.69	4.53	5.33	4.81

[1] Received too late to be included in general average.
[2] Precipitated at 5 cc concentration and used 15 cc of reagent.

Comments by Analysts.

B. E. Curry, Durham, N. H.: While our experience with this method is limited, and I realize that the chemicals involved may be had at much less expense than the platinic chlorid, at the same time it seems to me that this method is not an improvement over the old official method, as regards time, convenience, and accuracy.

P. L. McCreary and P. L. Hibbard, Berkeley, Cal.: For the volumetric method, filtration was performed on asbestos, supported on a perforated porcelain disk in a filter tube, thus having the same effect as a porcelain gooch, but more rapid and convenient. The sodium cobalti-nitrite solution was made up according to instructions in the circular letter and all determinations were made within 10 days of the time when the solution was ready. Our experience indicates that the volumetric method gives uncertain and incorrect results, and saves little time in comparison with the official platinum method. On account of the necessarily small amount taken, it is not suitable for the determination of high percentages. Variation in the amount of drying on the steam bath, length of time of standing before filtering, and volume of water used in boiling with potassium permanganate seemed to affect the results. The gravimetric cobalti method gives low and variable results, and besides has no advantage over the official platinum method except in the cost of reagent, which is not much, as the platinum is easily recovered while the cobalt is lost.

Cornelius Beatty, College Park, Md.: The gravimetric cobalti-nitrite method will take one-half an hour more time than the official method, since the precipitates must be dried at least one hour when the gravimetric cobalti-nitrite method is employed,

and only one-half an hour when the official method is employed. When the standard solutions have been made up in considerable quantities, tested, and delivered from stock bottles by siphons to overflow burettes, the volumetric cobalti-nitrite method will enable the analyst to make a given number of determinations in less time than by the official method or to finish a larger number of determinations in a day. In the matter of expense, both of the methods employing cobalt have the advantage of dispensing with the use of a platinum solution, and the volumetric cobalti-nitrite method has the additional advantage of eliminating the use of alcohol. The writer recommends the gravimetric cobalti-nitrite method (1) because he has obtained more accurate results by it than by the volumetric cobalti-nitrite method; (2) this method is less complicated and therefore less liable to accidental error than the volumetric cobalti-nitrite method; and (3) the cobalt solution may be used in large excess in either of the cobalti-nitrite methods, insuring the precipitation of all of the potash.

W. W. Murray, Baltimore, Md.: (*a*) In a laboratory like mine I do not believe, as the method now stands, that it offers any advantage over the present official method. The gravimetric method, if it can be made more reliable, might become a good check method. I do not believe that the volumetric method will appeal to the average commercial chemist. The briefer the method the less liability for error to enter in. (*b*) When the evaporation of the sample is completed I think that after cooling and adding cold water to dissolve the excess of cobalti-nitrite, it would be better to allow the sample to stand for at least an hour. This insures the complete solution of the excess of cobalti-nitrite and reduces the possibility of high results.

O. M. Shedd, Lexington, Ky.: On the whole, I believe that this method is a very promising one and if properly worked will give excellent results. From my own work I would recommend that the volume be concentrated to from 5 to 10 cc and then the acetic acid and 15 cc of nitrite added. The reason for recommending more nitrite is that when considerable potassium is present there is still a good excess of reagent present at the end which makes possible a clearer filtration. Finally, I believe that a pasty condition of the residue on cooling is the proper one to be desired to secure the most uniform results.

L. F. Whipple, Kingston, R. I.: The old method seems to be preferable to the new one, especially if the comparative expense of the reagents in the two cases is not considered. In the case of sample No. 3 the gravimetric cobalti-nitrite method exhibited some difficulty in the final filtering, this being a very slow process. It was likewise noticeable that there were impurities present in this precipitate which apparently were not removed by the wash solutions and, as you will observe by the results, probably resulted in too large amounts of precipitate.

Otto McCreary, Geneva, N. Y.: The method is shorter than the platinum method, and I think with a few changes can be made to be just as accurate. The variations in the results in the gravimetric method are due to the unstable nature of the cobalti-nitrite solution. On standing a number of days the solution gave high results.

H. H. Hill, Blacksburg, Va.: I think that the methods need further study before adoption. The only change I made was to evaporate nearly to dryness so that, after cooling, it had completely dried. I believe this makes a difference. In the volumetric method the asbestos was treated with permanganate solution, and afterwards with oxalic acid before using.

M. P. Sweeney, Geneva, N. Y.: The proposed method for extracting the potash by washing with hot water on a filter appears to be decidedly better than the present official method in that it gives a cleaner solution to work with and, in most cases, somewhat higher results. The proposed volumetric method, with care, gives very excellent results. The actual length of time during which the worker must give attention to the determination is greater than in the official method. The actual time required for making the complete test is, however, much less. If results are required on short notice, this method is very desirable. The proposed gravimetric method gave excellent results. It is short and simple. As compared with the official method, it saves time and the use of expensive reagents. The greatest care must be used in making up and keeping the solution of sodium cobalti-nitrite. This was the only difficulty I experienced. With the reagent in good condition and careful work, the results by either of the proposed methods should be accurate.

F. B. Carpenter,[1] *Richmond, Va.:* We made some determinations by the cobalti-nitrite method, but the results were not satisfactory and are not reported. It is possible that if we had become more familiar with the method the results would have been better, but I do not see that this procedure possesses any advantage over the platinic chlorid method. The determinations given were made by Mr. R. Henry, of this laboratory, and the following potash results reported are the average of two closely agreeing determinations. Official gravimetric method: Sample 1, 51.88 per cent; Sample 2, 12.86 per cent; Sample 3, 4.79 per cent. By the official gravimetric method,

modified according to the referee's suggestions, by weighing 5 grams upon a 12.5 cm filter paper, and washing with successive small portions of hot water, etc., Sample 3 gave 4.84 per cent.

G. F. Lipscomb,[1] *Clemson College, S. C.:* I determined the potash in the three samples of fertilizers, first, by the official method; second, by the Drushel volumetric cobalti-nitrite method, as sent out by the referee; third, by Drushel's method as carried out by O. M. Shedd. I obtained more satisfactory results by following the suggestions of Shedd; that is, by evaporating to a small volume before adding the nitrite reagent and acetic acid. The following are the results obtained by each method: Official method, muriate 51.95 and 52.00 per cent; kainite 12.74 and 12.70 per cent; complete 4.51 and 4.50 per cent. By Drushel's method as sent out by the referee, muriate 48.01, 50.47, and 48.31 per cent; kainite 12.12 and 12.22 per cent; complete 4.33 and 4.24 per cent. By Drushel's method as carried out by O. N. Shedd, muriate 50.98, 51.34, and 50.36 per cent; kainite 12.60, 12.70, and 12.55 per cent.

Discussion of Results.

The tabulated results show quite a range of variation. The methods tested seem to work well in the hands of most analysts, but some have apparently found difficulty in getting results which agree closely with those obtained by the official method. This may be partly due to inexperience, but there are unquestionably opportunities for errors to occur unless certain precautions are well understood. Briefly stated, these precautions are as follows: Before precipitation the potash solution should be neither too dilute nor too concentrated. Care should be taken to evaporate to a sirupy condition so that the solution becomes a thick paste on cooling. Evaporation to dryness should be avoided. Thorough washing with water is necessary. During the process of titration allow from 10 to 15 minutes between the appearance of the dark-colored precipitate and the addition of sulphuric acid, and from 3 to 5 minutes longer before oxalic acid is added.

With the gravimetric method there is a tendency to high results, due probably to the presence of some impurity which is not carried off by the wash water. Some analysts have, however, obtained very accurate results by this method. With the volumetric method this trouble does not seem to occur. A possible source of error is in the cobalti-nitrite reagent, which as now prepared is unstable and decomposes very quickly if exposed to sunlight, and slowly upon standing in the dark. This decomposition is hastened by the presence of acetic acid.[2] A portion of the reagent prepared in this laboratory in March, 1910, after five months' standing, the greater part of that time in the dark, was tested and it was found that decomposition had taken place to such a degree that to obtain reliable results by its use was impossible. Shedd suggests that this difficulty may be avoided by making up solutions of cobalt acetate and sodium nitrite and adding them separately at the time of precipitation. This point should be further studied.

Another source of error lies in the method of titration. The appearance of the dark-colored precipitate is by no means an indication that the oxidation of the potash precipitate is complete. After the solution appears to be ready for the addition of sulphuric acid and oxalic acid, small amounts of the yellow precipitate will often be noticed creeping up the sides of the beaker. This should be washed down and digestion continued for about 10 minutes longer. Owing to the use of such a small aliquot the variations in sample No. 1 appear to be greater than the actual error occurring in the determination. In calculation this error is increased ten times. The use of a larger aliquot should be studied.

The following additional determinations were made by O. M. Shedd, having the volume about 5 cc on adding the acetic acid and nitrite reagent. The amounts of nitrite used are indicated and the consistency of the residue noted.

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[1] Results received too late to be tabulated.

[2] Shedd, J. Ind. Eng. Chem., 1910, 2 (9): 379.

Additional potash determinations by O. M. Shedd, using a 5 cc concentration and varying amounts of nitrite.

Amount of nitrite used (cc).	Consistency on cooling.	Amount of potassium monoxid found.	Amount of nitrite used (cc).	Consistency on cooling.	Amount of potassium monoxid found.
		Per cent.			*Per cent.*
Muriate:					
10	Dry	51.591	C. P. potassium sulphate (theory 54.05 per cent of potassium monoxid):		
10	do	51.506			
15	do	52.223			
15	do	51.548			
15	do	51.694			
15	Very dry	51.420	15	Dry	53.817
15	Pasty	51.420	15	do	53.466
15	Thick paste	51.591	15	do	54.581
15	Very thin paste	51.343	15	do	54.527
25	Dry	50.949			
25	Pasty	51.078	Average		54.098
Kainite:			15	Pasty	53.902
15	Dry	12.556	15	do	53.988
15	do	12.724	15	do	53.988
15	Very dry	12.458			
15	Very thin paste	12.659	Average		53.959
25	Dry	12.710			
25	Pasty	12.689			

B. E. Curry reports the following potash determinations on two samples selected from their fertilizer inspection lot:

Sample No. 66: By the official method, 6.85 and 6.85; by the gravimetric cobalti-nitrite, 6.75 and 6.63; by the volumetric cobalti-nitrite, 6.60, 6.60, and 6.45 per cent.

Sample No. 73: By the official method, 7.40, 7.40, and 7.42; by the gravimetric cobalti-nitrite method, 7.35, 7.57, and 6.85 per cent.

For some reason, which at present is not known, we were unable to get any satisfactory results on this sample by the volumetric method. The results did not check within 1 per cent, and many of the figures varied by as much as 2 or 3 per cent.

In order to test more thoroughly the accuracy of the volumetric method as compared with the official when applied to a muriate, the following series of determinations was made by the referee:

Comparison of the volumetric method with the official method when applied to a muriate (sample No. 1).

[Results calculated in per cent on a 0.1 gram basis.]

Method used.	Potash (K_2O).	Method used.	Potash (K_2O).
	Per cent.		*Per cent.*
Series I: Official method	5.16	Series V: Proposed volumetric method, adding sulphuric acid and oxalic acid immediately upon the appearance of the dark-colored precipitate	5.02
	5.17		5.07
Average	5.17		5.05
Series II: Proposed volumetric method	5.15		
	5.18		
	5.08	Average	5.05
Average	5.14	Series VI: Volumetric method, using Shedd's suggestion of 5 cc concentration and 10 cc of reagent	5.38
Series III: Dilute 65 cc of potassium permanganate to about 300 cc, heat nearly to boiling; add yellow precipitate and digest about 10 minutes after appearance of dark precipitate	5.12		5.36
	5.16		5.31
	5.18	Average	5.35
Average	5.15	Series VII: 5 cc concentration and 15 cc of reagent	5.32
Series IV: Drushel's method as used in the work of 1909	5.17		5.24
	5.13		5.29
	5.12	Average	5.28
Average	5.14		

Series I, II, III, and IV show very close agreement on a 0.1 gram basis; but when calculated to 1 gram variations as great as 1 per cent occur. The trouble then appears to be largely in the small amount taken. Series V shows the danger of low results due to addition of sulphuric acid and oxalic acid too quickly after appearance of the dark precipitate. In series VI and VII the precipitate came down in a very finely divided state and filtered very slowly, thorough washing being difficult. This, I believe, accounts for the results being somewhat high. I have always had this experience when using too great a concentration. For proper filtration the precipitate should be granular in form, and should settle quickly when stirred with water.

In connection with the work on the modified official method reported by cooperating chemists, the referee made a study of 32 samples of mixed goods, collected in New York State, with the following results:

Comparison of potash (K_2O) determinations by the official method and its modification by washing 5 grams through a filter paper with hot water.

Sample number.	Official method.			Modified official.			Difference.
	Duplicates.		Average.	Duplicates.		Average.	
	Per cent.		*Per cent.*	*Per cent.*		*Per cent.*	
24	4.92	5.00	4.96	5.28	5.24	5.26	+0.30
56	6.90	6.92	6.91	7.10	7.06	7.08	+ .17
73	4.88	4.89	4.89	5.26	5.26	5.26	+ .37
88	7.20	7.10	7.15	7.10	7.20	7.15	+ .00
122	3.13	3.12	3.13	3.56	3.52	3.54	+ .41
123	3.80	3.78	3.79	3.96	3.92	3.94	+ .15
125	5.71	5.75	5.73	6.02	6.20	6.11	+ .38
154	3.13	3.11	3.12	3.50	3.52	3.51	+ .39
179	5.85	5.88	5.87	6.04	6.02	6.03	+ .16
183	9.10	9.07	9.09	9.18	9.20	9.19	+ .10
239	7.03	7.02	7.03	7.08	7.12	7.10	+ .07
301	8.47	8.43	8.45	8.54	8.46	8.50	+ .05
412	7.95	7.91	7.93	7.80	7.88	7.84	− .09
431	2.71	2.67	2.69	2.58	2.60	2.59	− .10
426	8.10	8.13	8.12	8.12	8.22	8.17	+ .05
429	8.60	8.58	8.59	9.00	9.00	9.00	+ .41
443	8.23	8.24	8.24	8.60	8.48	8.54	+ .30
476	8.62	8.58	8.60	8.58	8.56	8.57	− .03
503	3.51	3.51	3.51	3.70	3.66	3.68	+ .17
518	8.47	8.46	8.47	9.00	9.02	9.01	+ .54
519	2.14	2.08	2.11	2.16	2.16	2.16	+ .05
521	8.55	8.69	8.62	8.76	8.70	8.73	+ .11
550	8.05	8.07	8.06	8.00	8.20	8.10	+ .04
634	5.13	5.21	5.17	5.32	5.18	5.25	+ .08
627	5.50	5.48	5.49	5.68	5.62	5.65	+ .16
672	1.45	1.53	1.49	1.82	1.82	1.82	+ .33
702	9.01	8.99	9.00	9.24	9.26	9.25	+ .25
710	5.77	5.78	5.78	6.00	5.98	5.99	+ .21
712	3.30	3.30	3.30	3.38	3.38	3.38	+ .08
779	4.32	4.28	4.30	4.34	4.36	4.35	+ .05
806	6.69	6.69	6.69	6.56	6.72	6.64	− .05
827	8.21	8.09	8.15	8.60	8.58	8.59	+ .44

In this table only four samples show less potash by the modified than by the official method, the greatest loss being 0.1 per cent. One sample shows no difference and 27 samples give larger amounts of potash by the modified method, the increase ranging from 0.05 per cent to 0.54 per cent.

Conclusions.

By the volumetric method, as outlined, the majority of analysts have obtained satisfactory results. It is probable that the variations occurring in the muriate may be avoided by increasing the size of the aliquot. Although it is difficult to draw definite conclusions from the data received, from my experience with the method I think that with slight modification an accurate optional method can be developed. Of the two proposed methods the gravimetric is more simple and seems very promising.

Results obtained on the mixed fertilizer by the modified official method show an increase of potash recovered of from 0.1 to 0.3 per cent. Thirty-two different samples of mixed goods tested in this manner show a general increase over the amounts yielded by the official method.

In view of these facts, I recommend a study of the volumetric and gravimetric cobalti-nitrite methods for another year, and that a further trial be made of the modified official method by washing a weighed amount of the sample through filter paper with hot water and determining potash in the filtrate.

Mr. Bizzell, the associate referee on available potash, reported by letter that he had not been able to do any work on the subject and made the following statement in regard to this investigation:

Previous to the last meeting of the association I made some preliminary experiments on the recovery of potash from mixed fertilizers, with promising results, but I have been unable to continue the work this year and do not see any immediate prospect of being able to take it up again. I am of the opinion that with our present knowledge of soils we are not justified in attempting to devise laboratory methods for the determination of available potash. The loss of water-soluble potash when potash salts are mixed with acid phosphate should be further investigated.

A letter from Vice President Woll was read regretting his inability to be present owing to a recent operation.

Mr. Haskins called attention to the great desirability of the referees getting their samples for cooperative work out earlier in the year, especially in the case of the fertilizer chemists, whose heaviest work comes in the summer and who can not give much time to the association investigations unless the samples are received during the winter months.

REPORT ON SOILS.

By J. G. Lipman, *Referee.*[1]

At the meeting of the association in 1909 it was recommended that the Drushel modification of the cobalti-nitrite method in connection with the J. L. Smith fusion method be tested by the association the coming year as a method for total potassium. No other recommendations were made by the association, and the referee on soils felt at liberty, therefore, to suggest cooperative work on methods for determining acidity in soils. In making these suggestions he was prompted by the wish to enlist the interest and the aid of soil analysts, and to bring about, if possible, the adoption by the association of a reliable method for the quantitative estimation of soil acidity. That the need for such a method or methods is urgent need scarcely be emphasized here. All students of soil fertility recognize the importance of soil reaction as a factor in crop growth. They also recognize the fact that acid conditions prevail widely in the older soils of the United States.

In view of these facts the referee requested the volunteers in the association work to make a further comparison of the J. L. Smith and the modified cobalti-nitrite method,[2] as well as to make acidity determinations according to the Süchting and the Veitch methods. For this purpose three lots of soil, known to be acid, were secured by the referee through the kindness of B. L. Hartwell, of the Rhode Island station, and of J. W. Ames, of the Ohio station. On behalf of the association the referee wishes to thank these gentlemen for the service rendered. The three samples sent out were numbered 1, 2, and 3, respectively, the first being derived from the acid plots at Kingston, the second from the experiment fields at Wooster, and the third from those at Strongville.

[1] Presented by Mr. Cathcart, in the absence of the referee.

[2] U. S. Dept. Agr., Bureau of Chemistry Bul. 132, p. 21.

Determination of Total Potassium in Soils by the Smith and the Cobalti-Nitrite Methods.

ANALYTICAL RESULTS.

Determinations of potassium were made in the samples by O. M. Shedd, S. D. Averitt, P. E. Brown, E. Van Alstine (through J. H. Pettit), and W. B. Ellett. In some instances it was found necessary to recalculate the results in order to establish a uniform basis of comparison.

Comparison of the Smith and the modified cobalti-nitrite method for total potassium.

[Water-free basis.]

Analyst.	Soil I.		Soil II.		Soil III.	
	Smith method.	Cobalti-nitrite method.	Smith method.	Cobalti-nitrite method.	Smith method.	Cobalti-nitrite method.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
O. M. Shedd, Kentucky	1.796	1.881	1.574	1.655	1.889	1.948
S. D. Averitt, Kentucky	1.869	1.908	1.643	1.667	1.972	2.043
	1.770	1.908	1.527	1.694	1.929	2.134
	1.800	.....	1.594	.....	1.940	.....
Average	1.813	1.908	1.588	1.680	1.947	2.088
E. Van Alstine, Illinois	2.05	1.91	1.75	1.71	2.10	2.01
	1.98	1.90	1.76	1.74	2.09	1.97
	1.98	1.97	1.74	.....	2.11	1.88
Average	2.003	1.926	1.750	1.725	2.100	1.953
W. B. Ellett, Virginia	1.89	1.80	1.89	1.61	.....	.....
	1.93	1.76	1.83	1.51	.....	.....
Average	1.910	1.780	1.860	1.560	.....	.....
P. E. Brown, New Jersey	1.754	1.835	1.558	1.594	1.847	1.855
	1.766	1.783	1.589	1.620	1.872	1.842
	1.731	1.835	1.572	1.620	1.872	1.881
	1.784	.....	1.583	.....	1.894	.....
Average	1.759	1.813	1.575	1.611	1.871	1.859
General average	1.854	1.863	1.739	1.642	1.956	1.951

Apart from the results recorded in the table, Mr. Van Alstine made some preliminary determinations by the cobalti-nitrite method on material from the same fusions used for the J. L. Smith method. He obtained for Soil I, 2.02, 1.99, and 2.20 per cent; for Soil II, 1.92, 1.68, and 1.83 per cent; and for Soil III, 2.24, 2.34, and 2.14 per cent. Additional determinations were made also by Mr. Ellett on Soils I and II; he found, by the J. L. Smith method, 2.09 per cent in Soil I and 1.82 per cent in Soil II.

COMMENTS BY ANALYSTS.

J. H. Pettit, Illinois: In Mr. Van Alstine's opinion the cobalti-nitrite method can be run successfully with practice, but there is a question as to whether or not it has any advantage over the platinic-chlorid method, while it offers more opportunities for error in its manipulation.

O. M. Shedd, Kentucky: In the work, 1 gram portions were used in the fusion which was afterwards divided and one-half gram aliquots used for the regular J. L. Smith method and for the cobalti-nitrite method. By this procedure I have eliminated the error of the fusion and have been able to compare the two methods from the same solution. The plan followed in the volumetric method was to slightly acidify the solution (one-half the filtrate from the fusion) with acetic acid, evaporate to about 5 cc, add 5 or 6 drops of acetic acid and 15 cc of recently prepared nitrite reagent. This

was then evaporated on a water bath until nearly dry on cooling, which required about 40 minutes. These residues were heated perhaps a trifle too long; recent work on other samples shows that, by regulating the volume as indicated, a time limit of from 30 to 35 minutes should control the evaporation, and the residues should be pasty on cooling. As a rule, prolonged heating has a tendency to give high results, due to carrying down an excess of the sodium cobalti-nitrite, which is not removed in the washing and which reacts with permanganate.

S. D. Averitt, Kentucky: In the determination of total potassium in Soils I and II, 1 gram was fused over the blast and divided for the Smith and cobalti-nitrite methods, and in Soil III, one-half gram was fused with a specially arranged Bunsen for the gravimetric determination. The rather low gravimetric results on Soil II are attributed to loss when burning off the ammonia salts. The volumetric method has several points in its favor, the main being the time saved. The work of last year shows concordant results agreeing closely with the Smith method. The work done in this laboratory this year on the volumetric method is in agreement with that done heretofore.

COMMENTS BY REFEREE.

The comments just cited, together with the results as reported, are not unfavorable to the cobalti-nitrite method, which, however, gave higher results in the hands of Shedd and Averitt, and lower results in the hands of Van Alstine and Ellett. The best agreement between the Smith and cobalti-nitrite methods is shown by Brown; however, his results are lower than the average of all of the analytical data. Everything considered, the two methods agree very well, and the cobalti-nitrite method should, therefore, prove acceptable as an optional official method for the determination of total potassium in soils.

Determination of Soil Acidity by the Veitch and Süchting Methods.

Among the various methods that have been devised for the quantitative estimation of acidity in soils there is none that has given uniformly satisfactory results. The method proposed by Veitch [1] some years ago has been used to a considerable extent in this country, notably by Blair and Macy,[2] in their study of the lime requirements of Florida soils. More recently a new method was proposed by Süchting,[3] who has also published a critical discussion [4] of other methods.

After careful consideration of the several methods available for acidity work the referee decided to institute a comparison of the Süchting and Veitch methods. Accordingly, the following instructions were sent out together with the soil samples.

Veitch's method for determining acidity in soils—Determination of soil reaction.—Place approximately 10 grams of the soil in a 100 cc Jena Erlenmeyer flask, cover with approximately 100 cc of neutral distilled water, stopper, shake vigorously at intervals and allow to stand overnight. Decant about 50 cc of the clear supernatant liquid into a small Jena beaker, add a few drops of phenolphthalein solution and boil until the appearance of the pink color, or to a volume of about 5 cc. If the solution becomes pink, the soil is alkaline in reaction; if it remains colorless, the soil is neutral or acid in reaction.

Determination of lime requirement.—To three portions of soil (each consisting of as many grams as the standard limewater contains tenth milligrams of lime (CaO) per cubic centimeter) add 50 to 60 cc of distilled water and different amounts of standard limewater. For example, to the first add 10 cc, to the second 20 cc, and to the third 30 cc of limewater. Dry down at once on the steam bath, transfer to stoppered Jena flasks with 100 cc of neutral distilled water, allow to stand overnight, with occasional shaking; draw off 50 cc, place in a Jena beaker, add a few drops of phenolphthalein solution, and boil until the appearance of the pink color, or in case no color is developed to a volume of about 5 cc. Then, with two portions of treated soils as guides, one of which has been rendered alkaline by the limewater and the other of which is still acid, prepare three fresh portions of soil and add limewater as before, except that the amount added to one portion differs from that added to another by 1 to 2 cc. Dry, take up with 100 cc of water, allow to stand, draw off, and treat exactly as before. The smallest amount of limewater which gives the characteristic pink color is taken as the

[1] J. Amer. Chem. Soc., 1902, 24: 1120; 1904, 26: 637.
[2] Florida Agr. Exper. Sta. Bul. 93, May, 1908.
[3] Zts. angew. Chem., 1908, 21: (4): 151.
[4] Landw. Versuchs-Stat., 1909, 70: 13.

lime equivalent of the soil. Each cubic centimeter of standard limewater is equivalent to a lime requirement of 0.01 per cent, expressed as calcium oxid. It is essential that the distilled water used be free from alkalis and acid.

Süchting's method for determining acidity in soils.—When humic acids react with calcium carbonate, carbon dioxid is set free. The reaction does not stop here, however, for the calcium carbonate leads to further decomposition of the organic matter and the evolution of carbon dioxid. This impairs the accuracy of the Tacke[1] method, and Süchting[2] proposes, therefore, that after the acid soil has reacted with calcium carbonate for a certain length of time hydrochloric acid should be added, and the carbon dioxid evolved from the residual calcium carbonate determined. The amount of carbon dioxid originally present in the calcium carbonate being known, the acidity of the soil examined is readily calculated from the data obtained. The apparatus for carrying out the determination is set up as shown in the accompanying diagram, except that flask *c* is also provided with a stirrer. The entire apparatus is fastened to a stand.

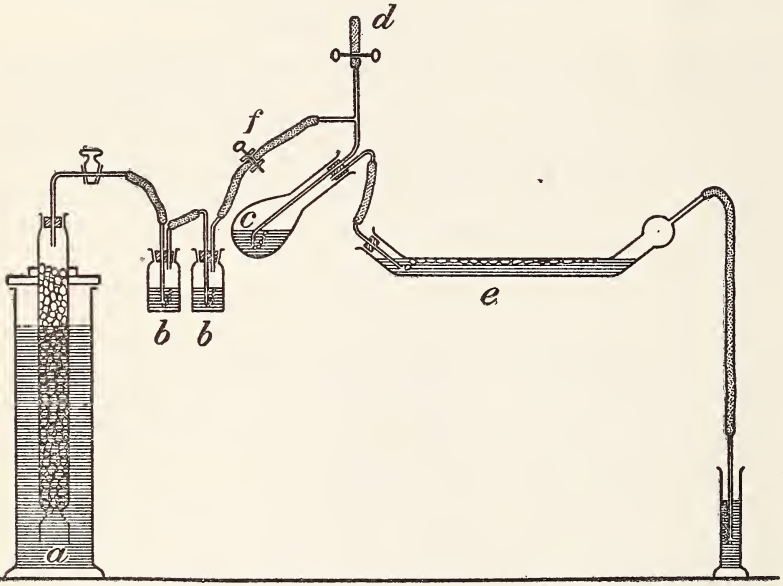

FIG. 2.—Apparatus for measuring the evolution of carbon dioxid for the determination of soil acidity. *a*, Hydrogen generator. *bb*, Acid and alkali for washing hydrogen. *c*, Reaction flask for soil and calcium carbonate. Capacity of *c*, 300 cc. *d*, Attachment for running in acid. *e*, Pettenkofer absorption apparatus. *f*, Pinch-cock for regulating flow of gas.

The operation is carried out by placing from 10 to 30 grams of soil in flask *c*, adding about 150 cc of freshly boiled water and a slight excess of calcium carbonate. The apparatus is then put together, and a slow current of hydrogen passed through it (about 6 to 10 bubbles per second). After two hours during which the contents of *c* are constantly being stirred, flask *c* and absorption apparatus *e* are shut off by means of pinch cocks, and 100 cc of tenth-normal sodium hydroxid introduced into *e*. By means of a funnel tube at *d* an excess of 20 per cent hydrochloric acid is added and carbon dioxid removed by passing hydrogen through the apparatus for one hour; at the same time stir the contents of *c*. Transfer the contents of *e* to a flask, add a solution of barium chlorid, and titrate the liquid against tenth-normal hydrochloric acid with phenolphthalein as an indicator. The amount of carbon dioxid found represents the calcium carbonate equivalent that did not react with the humic acids in the soil.

[1] Chem. Ztg. 1897, 21: 174. [2] Loc. cit.

ANALYTICAL RESULTS.

Data on the determination of acidity in the samples sent out by the referee were reported as follows:

Comparison of the Veitch and Süchting methods for soil acidity.

[Lime requirements in terms of calcium oxid.]

Analyst.	Soil I.		Soil II.		Soil III.	
	Veitch method.	Süchting method.	Veitch method.	Süchting method.	Veitch method.	Süchting method.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
P. E. Brown, New Jersey	0.465	0.151	0.158	0.076	0.298	.....
	.....	.146	.....	.076	.....	.....
	.....	.....	.....	.071	.....	.....
	.....	.....	.....	.066	.....	.....
	.....	.....	.....	.085	.....	.....
Average	.465	.148	.158	.075	.298	.....
S. D. Averitt, Kentucky	.290	.....	.110	.....	.150	.....
	.420	.....	.....	.....	.150	.....
Average	.355	.....	.110	.....	.150	.....
E. Van Alstine, Illinois	.821	.345	.810	.172	.306	0.203
	.....	.340	.....	.158	.....	.153
	.....	.350	.....	.192	.....	.225
Average	.821	.345	.810	.174	.306	.194
E. C. Carlyle, Texas	.092	.....	.042	.....	.042	.....
W. B. Ellett, Virginia	.370	.....	.150	.....	.120	.....

COMMENTS BY ANALYSTS.

S. D. Averitt, Kentucky: The Veitch, or limewater, method was given a very thorough test and I have satisfied myself that it is at best entirely unreliable as to results and too wasteful of time and energy to ever be of any value as a working method. The figures reported represent the best I can do working according to instructions.

G. S. Fraps (for E. C. Carlyle), Texas: Suggestions: (1) Require a test of the water to be used for making the acidity test. Boil 100 cc of distilled water to 5 cc with the addition of a few drops of phenolphthalein and see whether it is acid or not.

(2) Reduce the quantity of water used in the first treatment of the soil from 50 cc to 10 cc. I have not had time to test this point, but it appears to me that the evaporation on the water bath is liable to decompose calcium or magnesium silicates with a production of alkalinity. The use of 50 cc of water also lengthens the process considerably. In fact, the question of whether any evaporation at all is necessary might well be tested. If the soil absorbs lime for the neutralization of acidity very rapidly, it is probable that evaporation is not needed. If the absorption takes place slowly and 50 cc of water is used, there is a possibility of carbonate of lime separating out on the sides of the dish at the same time that it is needed to correct acidity. These suggestions are merely submitted for discussion and consideration, especially by the originator of the method.

J. H. Pettit, Illinois: In the Süchting method for the limestone requirement a Kjeldahl flask was used and so arranged that the whole flask could be thoroughly shaken during the running. The arrangement proved satisfactory. The carbon dioxid was finally absorbed in a regular potash bulb and weighed, this manipulation proving more satisfactory than the titration. A blank run with chemically pure calcium carbonate by this manipulation gave theoretical results. We found the Süchting method rather "langweilig" and were not able to get agreeing results in all cases. I have included for your information results obtained on these soils by our method. It shows a very marked variation which we are not yet able to explain. It was a surprise to me that the agreement with Süchting's method was not better. Upon other soils the agreement with the Veitch method is usually much closer. The additional results, which were obtained with the Hopkins and Pettit method, were as follows: Calcium oxid requirement, Soil I, 0.044 and 0.044 per cent; Soil II, 0.018 and 0.017 per cent; Soil III, 0.016 and 0.016 per cent.

Recommendations.

The results and comments, taken together, show that the acidity determinations are variable and contradictory and that there is great need for a reliable method for determining soil acidity. It is hoped that the search for such a method will be continued by the association, and the following recommendations are made:

It is recommended—

(1) That the modified cobalti-nitrite method be made an optional official method for the determination of total potassium in soils.

(2) That the study of methods for the quantitative estimation of soil acidity be continued.

REPORT ON INORGANIC PLANT CONSTITUENTS.

By O. M. Shedd, *Referee.*

Plan of Work.

The work on this subject for this year has been carried on according to the recommendations outlined by the referee in 1908 and subsequently changed by the association concerning the work for 1909. As no report was made to the association at the last meeting, the present referee was instructed to resume the work proposed for 1909.

The customary letter asking for cooperation was sent by the referee in January to all of the experiment stations and to several other analysts who have assisted in the work in the last few years. Samples were sent to 25 who expressed a desire to cooperate and results have been received from 14 who have completed all or some part of the work as outlined.

The methods studied were the peroxid method for sulphur in plants and a method for the separation of ferric and aluminic oxids in an ash solution. Two samples, graham flour and linseed meal, were sent for the determination of sulphur. For the method for the separation of ferric and aluminic oxids a synthetic hydrochloric acid solution was sent which represented an ash of the following composition:

	Per cent.
Potassium oxid (K_2O)	20.00
Sodium oxid (Na_2O)	.80
Calcium oxid (CaO)	30.00
Magnesium oxid (MgO)	10.00
Ferric oxid (Fe_2O_3)	2.00
Aluminic oxid (Al_2O_3)	3.98
Manganese oxid (Mn_3O_4)	.50
Phosphorus pentoxid (P_2O_5)	9.70
Sulphur trioxid (SO_3)	1.00

(Carbon dioxid, silica, chlorin, etc., were not taken into account.)

This ash solution was made from chemicals previously tested by the referee, the iron and aluminium being obtained from pure iron wire and sheet aluminium of known composition. The peroxid method as outlined by the referee is practically the same as the provisional method given in Bulletin 107, Revised, page 23. The method sent out for the separation of ferric and aluminic oxids is, with a slight modification, the same as that given in the proceedings of the association for 1908, Bulletin 122, page 93. The following additional directions were given in connection with the sulphur method:

Before or during the precipitation with barium chlorid the chlorin in the solution should be expelled, as this tends to interfere with the barium sulphate precipitation. It is better to allow to stand for 24 hours, as the large amount of sodium chlorid in the solution also retards the precipitation.

Make blank determinations on chemicals used, as it is difficult to obtain peroxid free from sulphate.

As the sulphur content of these samples is not high, it is advisable to use 2.5 grams of material for the fusion.

The method for the separation of ferric and aluminic oxids recommends the use of 50 cc aliquots corresponding to 0.50 gram of ash; removing the phosphoric acid *by precipitation with ammonium molybdate at a temperature not exceeding 40° C.*, and making blank determinations with all chemicals used. Otherwise the methods were the same.

The results reported by the collaborating chemists are as follows:

Analytical Results.

Cooperative results on sulphur in plants by the peroxid method.

Analyst.	Graham flour (SO_3).	Linseed meal (SO_3).
	Per cent.	*Per cent.*
W. H. Ross, Tucson, Ariz.	0.415	0.857
	.357	.748
	.466	.785
Average	.413	.797
Firman Thompson, Newark, Del.	.339	.853
	.377	.913
	.339	.832
Average	.352	.866
W. H. Peterson, Madison, Wis.	.454	.952
	.442	.911
	.474	.949
Average	.457	.937
R. O. Baird, Stillwater, Okla.	.388	.899
	.350	.899
	.408	.858
	.370	.861
	.367	.823
	.....	.864
Average	.377	.867
O. M. Shedd, Lexington, Ky.	.394	.827
	.381	.833
	.381	.823
	.374	.820
	.364	.....
Average	.379	.826
W. H. McIntire, State College, Pa.	.383	.875
	.367	.824
Average	.375	.850
F. W. Sherwood, West Raleigh, N. C.	0.352	0.695
	.343	.714
	.285	.731
	.305	.692
Average	.321	.708
A. T. Charron, Ottawa, Canada	.470	.922
	.463	.926
Average	.467	.924
J. P. Aumer, Urbana, Ill.	.340	.853
	.353	.833
	.345	.....
Average	.346	.843
O. B. Winter, East Lansing, Mich.	.391	.885
	.353	.858
	.357	.858
	.391	.947
Average	.373	.887
R. M. Pinckney, Bozeman, Mont.	.412	.699
	.412	.789
	.378	.830
	.306	.....
Average	.377	.773
G. E. Boltz, Wooster, Ohio.	.394	.874
	[1].390	[1].867
General average	[2].381	[3].841

[1] By method as outlined by Schreiber in U. S. Dept. Agr., Bureau of Chemistry Cir. 56, p. 9
[2] 39 determinations.
[3] 37 determinations.

Cooperative results on separation of ferric and aluminic oxids.

[Synthetic ash solution containing 2 per cent of ferric and 3.98 per cent of aluminic oxid.]

Analyst.	Ferric oxid (Fe_2O_3).	Aluminic oxid (Al_2O_3).	Analyst.	Ferric oxid (Fe_2O_3).	Aluminic oxid (Al_2O_3).
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
W. H. Ross, Tucson, Ariz.	1.98	4.48	O. B. Winter, East Lansing, Mich.	[2] 2.60	3.80
	1.98	4.46		[2] 2.52	3.64
	1.98	4.44		.....	3.80
Average	1.98	4.46		.....	3.60
H. D. Eggers, Newark, Del.	1.96	4.50	Average	2.56	3.71
	1.96	4.90			
	1.96	4.42	J. P. Aumer, Urbana, Ill.	[2] .70	[2] 6.15
	1.94	.....		[2] .76	[2] 5.55
Average	1.96	4.61	Average	.73	5.85
R. O. Baird, Stillwater, Okla.	2.16	3.50	G. E. Boltz, Wooster, Ohio.	1.94	4.05
	2.16	3.46		2.04	[3] 4.10
	2.16	3.48			
Average	2.16	3.48	Average	1.99	.....
O. M. Shedd, Lexington, Ky.	2.00	4.04	R. M. Pinckney, Bozeman, Mont.	1.92	[2] 5.35
	1.99	4.06		1.78	[2] 5.53
	2.02	4.06		1.78	[2] 5.53
	2.02	4.04		.....	4.57
	2.02	.....		.....	[2] 5.07
				.....	[2] 5.15
Average	2.01	4.05		.....	[2] 5.11
W. H. McIntire, State College, Pa.	2.14	3.92	Average	1.83	5.19
	.....	[1] 4.86	E. S. Erb, State College, Pa.	11.06	
				11.20	
Average	2.14	4.39	Average	11.13	
J. S. Jones, Moscow, Idaho.	2.28	4.28			
	2.28	4.16	A. T. Charron, Ottawa, Canada.	6.28	
	2.28	4.20		6.04	
				6.16	
Average	2.28	4.21	Average	6.16	
F. W. Sherwood, West Raleigh, N. C.	2.10	4.22			
	2.06	4.08	General average	[4] 2.04	[5] 4.12
	2.07	.....			
Average	2.08	4.15			

[1] Phosphoric acid (P_2O_5) present in the ignited precipitate.
[2] Omitted from general average.
[3] Aluminium determined as phosphate ($AlPO_4$).
[4] Average of 27 determinations.
[5] Average of 26 determinations.

Recommendations and their Discussion.

Objections have been made to the peroxid method on the ground that the material ignites in the fusion and also has an offensive odor, but the procedure seems to have given general satisfaction, and several of the analysts have recommended it.

Some of the high results obtained by the method for the separation of ferric and aluminic oxids, the referee feels, are due to not following the directions carefully, as will be explained later. For this reason, it was thought best that the work along this line should be continued next year, in order to clear up this point, otherwise the method would be recommended to be made official as was done by the referee in 1908.

The recommendations for the work next year are as follows:

1. That the peroxid method for sulphur in plants be made official.

2. That the method for the separation of ferric and aluminic oxids be made a provisional method and further work be done on it next year. That the referee next year should emphasize in the directions that the solution should never be concentrated nor, in fact, heated over 40° C.

3. That the referee for next year endeavor to find another method for these separations, and, if a satisfactory one is obtained, that cooperative work be done with it on a synthetic ash solution. In this connection it is recommended that the referee continue the work on the modified Gladding method as given in this report.

In regard to these recommendations, the referee might state that the peroxid method has been before this association since 1903. Since that time cooperative work has been done on this method for five years by 24 different analysts who have made 179 determinations upon nine different samples with a sulphur content ranging from about 0.30 per cent to 7 per cent of SO_3. With the exception of one sample, the results were entirely satisfactory, and not a single determination had to be omitted from the average. The sample above mentioned, on which low results were received, was a sample of mixed oils containing a known amount of artificial oil of mustard or allyl thiocyanate. The referee who had charge of the work during that year stated that he selected this substance that the actual sulphur content might be known, but that his selection was unfortunate in that its volatility was so great that the results obtained on it by the peroxid method could not be considered as a fair test.

The method was recommended in 1906 and 1907 to be made official, but no action has been taken by the association. No work was done on it in 1908 and 1909. The referee believes it is a good method and some action should be taken by the association this year.

The method for iron and aluminic oxids is also a good method and will ordinarily be found satisfactory. Some of the high results are due to the fact that the directions were not strictly followed. For instance, in two or three cases, the filtrates from the phosphoric acid separation were concentrated. This should never be done as molybdic acid separates and vitiates the results. Next year this point should be emphasized in the directions.

In regard to the third recommendation, the referee, the associate referee (W. H. McIntire), and E. S. Erb have done some work on the method published by R. F. Hare in the Journal of Industrial and Engineering Chemistry, January 1910, page 27. The method in brief consists in adding a known excess of ferric chlorid ($FeCl_3$ $6H_2O$), or more than is necessary to combine with the phosphoric acid present, and then separating the iron and aluminium by the acetate method. The precipitate is redissolved and precipitated by ammonium hydrate. Knowing the amount of ferric oxid added, and estimating the phosphoric acid and ferric oxid, the difference between the sum of these three and the total precipitate, should represent the alumina in the solution. This was thought to be a promising method, as it fits in with the general scheme of ash analysis, and if found to be satisfactory would shorten the work considerably.

Several determinations have been made on the synthetic solution by adding different amounts of ferric oxid as ferric chlorid, but in every case the results obtained for alumina have been too low and this has been shown to be due to iron, aluminium, and principally to phosphoric acid, being carried through in the washings, probably due to the hydrolyzation of the phosphate.

The referee, in several determinations, has worked over the filtrates and washings in the method and obtained sufficient ferric oxid, alumina, and phosphoric acid to make the alumina obtained in this manner agree very closely with the amount present. In this work the amounts of sodium acetate used were changed in the different determinations in an effort to secure the right conditions. The most serious loss is due to the phosphoric acid which in one case amounted to 11 per cent of the amount present.

The percentages of alumina obtained by adding the different amounts of ferric oxid as ferric chlorid ($FeCl_3\ 6H_2O$) to the solution are given in the following table:

Alumina results obtained on adding varying amounts of ferric chlorid.

[Synthetic ash solution containing 2 per cent of ferric oxid and 3.98 per cent of alumina.]

Analyst.	Ferric oxid added as ferric chlorid.	Sodium acetate used.	Aluminic oxid found.	
			First determination.	After working over filtrate and washings.
	Grams.	*Grams.*	*Per cent.*	*Per cent.*
W. H. McIntire, State College, Pa	0.1485	.....	3.02	.....
	.1017	.....	3.68	.....
	.0670	.....	2.86	.....
	.0386	.....	2.44	.....
E. S. Erb, State College, Pa	.1017	.....	3.60	.....
O. M. Shedd, Lexington, Ky	.4112	1	2.80	4.40
	.4112	4	3.36	4.30
	.2056	3	2.38	3.80
	.2056	2	2.50	3.94
	.2056	1	3.02	.....

An objection that could be raised against this method, even if satisfactory otherwise, would be that large amounts of ferric oxid are added to obtain, in some cases, very small amounts of alumina. But the defect in the method illustrated by the table makes it unnecessary to consider it further for work of this kind.

Some work has been done by the referee on the synthetic ash solution by using a modification of the Gladding oxalate method, as given in the Journal of Industrial and Engineering Chemistry for April 1909, page 249. The method as given was intended for phosphate rocks, in which the amount of phosphoric acid in proportion to the ferric oxid and alumina is ordinarily much larger than in an ash solution. It was thought that by adding an excess of ammonium phosphate to the solution this method could be made applicable for the estimation of ferric oxid and alumina in an ash solution, provided other substances did not interfere.

In the synthetic solution used there was an excess of phosphoric acid compared with the ferric oxid and alumina present to form the phosphates of these bases. To see if this excess was sufficient, two determinations were made and 3.61 per cent and 3.54 per cent of alumina (Al_2O_3) were obtained in the respective determinations.

As Gladding had stated that a large excess of phosphate was necessary, the plan was tried of adding 1 gram of ammonium phosphate to the solution. The results obtained were 4.10 per cent and 4 per cent of alumina. Paper pulp had been added to the phosphate on precipitating and the precipitates obtained were readily mixed with potassium hydrogen sulphate and fusions made for iron determinations. Zinc was used as a reducing agent and the iron titrated with tenth-normal potassium permanganate. The results obtained were 2 per cent and 2.06 per cent of ferric oxid.

As the method seemed to work so well on this solution, the plan was tried of adding known amounts of manganese sesquioxid (Mn_3O_4) and of magnesium oxid to the solution to see if these bases would influence the results. To an aliquot of 0.5 gram of the ash was added 0.25 gram of anhydrous manganese chlorid, which with the amount of manganese sesquioxid already present in the solution made an equivalent of 30.8 per cent of manganese sesquioxid present. The result gave 4.36 per cent of alumina. To another 0.5 gram aliquot was added 0.25 gram of magnesium oxid, which with the magnesium oxid already present made an equivalent of 60 per cent of magnesium oxid. The result gave 4.29 per cent of alumina.

The method seems very promising for these separations, as other bases apparently do not interfere, but lack of time has prevented the referee from continuing the work along this line at present. For convenience the method pursued in this work is summarized as follows:

Use 50 cc (0.5 gram) of the sample and if the iron has not been already oxidized add a few cubic centimeters of hydrogen peroxid and boil for a few minutes to oxidize the iron and expel oxygen. Add ammonium hydroxid until a precipitate begins to form, then hydrochloric acid until just clear, then 1 gram of oxalate of ammonium in crystals, and boil gently for a short time, shaking occasionally to avoid bumping. Let settle and filter from precipitated oxalate of lime into a 500 cc Kjeldahl flask, add 5 cc of concentrated sulphuric acid and evaporate to white fumes to destroy excess of oxalic acid. (This boiling down and destruction of oxalic acid can be done in twenty minutes and during the first part of the boiling care should be taken to prevent bumping). Cool, add 1 gram of ammonium phosphate, 50 cc of water and 5 cc of strong hydrochloric acid. Boil gently a few moments to dissolve any dehydrated sulphate of iron, boiling until the solution is clear. Rinse into a beaker, make up to about 150 cc and precipitate the iron and alumina as phosphates by adding ammonium hydroxid until a precipitate begins to form, just clearing with hydrochloric acid, and then adding 25 cc of ammonium acetate solution (sp. gr. 1.04). Or if preferable, the solution can be treated as in the Kjeldahl flask (just described) and poured in a thin stream into the acetate solution, using sufficient water in the rinsing to bring the total volume to that indicated above. A small amount of finely divided quantitative paper pulp is added to the phosphates to insure that they will be finely divided after the ignition and be readily fused with potassium bisulphate for the iron determination. The phosphates are heated from one-half to one hour at 60° C., filtered and washed with boiling hot nitrate of ammonia solution (2.5 per cent). Carefully ignite the precipitate without removing from the paper, at first with low flame until the paper is charred and gradually increase until all of the carbon has gone and finally blast for a minute. Deduct the iron phosphate present and multiply the remainder by 0.418 to obtain the alumina.

If the precipitate has been treated as indicated, the iron oxid can be readily determined by fusion with potassium bisulphate, cooling, adding concentrated sulphuric acid, and heating to boiling. Transfer to a flask, add water, and digest until all sulphate is in solution. Reduce with zinc, and after this has been acted upon by the acid present and the reduction is complete, cool, and titrate with standard potassium permanganate.

Mr. Shedd presented the following recommendations relating to soil methods, which were referred to Committee A for consideration:

(1) That the referee on soils for 1911 be instructed to investigate a more accurate method for humus determination.

(2) That the official method for manganese in soils, page 15 of Bulletin 107, revised, be changed to read as follows, in order to restore the original procedure as given in Bulletin 46, revised:

Concentrate solution B to about 50 cc, cool, add bromin water until the solution is colored, make alkaline with ammonium hydroxid, and heat to boiling in a covered beaker, etc.

The object of the change is to insure that the solution is ammoniacal during boiling, which is necessary to bring down the manganese.

President Withers announced the following committee on nominations: William Frear, Pennsylvania; C. G. Hopkins, Illinois; and B. W. Kilgore, North Carolina.

Mr. Hopkins called attention to the desirability of always reporting the total amount of the various constituents in soils and fertilizers in connection with the so-called available or acid-soluble constituents, in order to provide data upon which to base a just estimate of the material and its usefulness.

The association adjourned until 1.30 p. m.

THURSDAY—AFTERNOON SESSION.

REPORT ON INSECTICIDES.

By C. C. McDonnell, *Referee.*

The cooperative work on insecticides this year has been limited to work on lead arsenate, London purple, and potassium cyanid. Results were reported from six laboratories in addition to the work done in the Bureau of Chemistry.

Lead Arsenate.

For the past three years the referee has given especial attention to methods for analyses of lead arsenate. The most study has been given to the methods proposed by Haywood in 1906 and adopted provisionally by the association in 1907, (Bulletin 107, Revised, p. 239). It has been found that the method for total arsenic gives very satisfactory results, even in the hands of those who have had no previous experience with it. The method for soluble arsenic can be modified in that the ten-day period for extraction of arsenic may be very materially reduced. The method for total lead gives very good results on pure lead arsenate, if carefully carried out, but in the presence of certain impurities such as lime, which some commercial samples contain, the method requires some modification.

The cooperative work this year consisted of the study of the following determinations: Moisture, total lead and arsenic oxids, and soluble arsenic oxid, according to methods given in Bureau of Chemistry Bulletin 107, Revised, pages 239 and 240.

In addition, another method was proposed for lead as follows:

Lead oxid, Method II.—Use 50 cc of the solution prepared as in the previous method for total lead oxid; add ammonium hydroxid until a permanent precipitate begins to form, then add a few drops of nitric acid to redissolve the precipitate. Run hydrogen sulphid into the solution, in the cold, until the lead is all precipitated; filter off the precipitate containing the lead sulphid and wash with hydrogen sulphid water. Dissolve the lead sulphid in nitric acid (using from 15 to 20 cc of a mixture of equal volumes of concentrated acid and water), add to this solution 3 cc of concentrated sulphuric acid; evaporate in a porcelain dish and heat on a hot plate till white fumes appear and all nitric acid has been expelled. From this point proceed as indicated under Method I.

The sample submitted for the work was prepared by the referee by thoroughly mixing the following: 900 grams of pure lead arsenate, 50 grams of pure dry calcium arsenate, 30 grams of pure calcium carbonate, and 20 grams of pure dry sodium arsenate.

The results reported are given in the following table:

Cooperative results on lead arsenate.

Analyst.	Moisture.	Total arsenic oxid (As_2O_5).	Total lead oxid (PbO).		Water-soluble arsenic oxid (As_2O_5).
			Method I.	Method II.	
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
R. J. Davidson, Blacksburg, Va	.....	32.10	.....	.....	.....
	.....	32.17	.....	.....	.....
H. S. Stahl, Blacksburg, Va	.....	32.30	.....	.....	.....
	.....	32.37	.....	.....	.....
C. E. Bradley, Corvallis, Oreg	0.08	32.14	63.64	60.00	6.87
	.08	32.09	63.80	60.18	6.87
H. R. Watkins, Washington, D. C	.09	32.00	63.60	58.68	5.92
	.....	32.00	63.21	58.70	.....
Mattie E. Storer, Berkeley, Cal	.23	31.10	65.21	57.70	5.14
	.23	31.37	64.91	58.09	5.30
	.....	31.31	65.01	55.12	5.30
	.....	31.46	64.87	54.87	.....
	.....	31.17	.....	60.64	.....
	.....	.....	.....	58.09	.....
T. E. Keitt, Clemson College, S. C	.30	32.20	64.08	59.88	6.18
	.....	32.16	64.10	59.70	6.18
	.....	32.13	63.98	.....	.....
	.....	32.09	.....	.....	.....
W. D. Lynch, Washington, D. C	.12	31.91	64.19	58.95	6.41
	.12	31.91	64.15	59.12	6.35
R. C. Roark, Washington, D. C	.32	31.98	64.79	58.34	6.40
	.31	31.62	64.15	58.99	6.14
	.....	31.78	64.76	59.92	.....
W. B. Pope, Washington, D. C	.29	31.88	64.30	59.25	6.25
	.29	31.88	64.26	59.35	6.14
C. C. McDonnell, Washington, D. C	.28	31.89	64.63	59.40	.....
	.27	32.02	64.30	59.45	6.36
	.....	.....	64.50	59.75	6.50
	.....	.....	64.58	59.53	.....
Average	.22	31.88	64.32	58.81	6.14

In the case of the low results reported on moisture the drying was probably not carried to constant weight.

The results given on total arsenic oxid are very good. This method has proved satisfactory for the past three years, and the referee renews the recommendation made last year, which was approved and referred to the association for final action this year, that this procedure be adopted as an official method for total arsenic oxid in lead arsenate.

The results on lead oxid by Method I are of course too high, owing to the presence of calcium in the sample, and it is evident that this can not be recommended as an official method for the determination of lead in commercial lead arsenate.

The results by Method II, while not agreeing as closely as might be desired, more nearly represent the amount of lead oxid in the sample. This method is long and disagreeable in some respects, but if certain precautions are observed it will give good results. It was found that on treating the lead sulphid precipitate on the filter with 1:1 nitric acid, the results were sometimes low, due to the oxidation of some of the lead sulphid to the sulphate which remained on the filter. More satisfactory results were obtained by treating the filter containing the lead sulphid precipitate in a beaker with about 50 cc of 1:2 nitric acid and digesting on the steam bath for an hour. This was then filtered, washed thoroughly, and evaporated, after the addition of 3 cc of concentrated sulphuric acid, in a porcelain dish, and the lead sulphate determined as directed.

A method for determining lead as the chromate has been worked out, and is described in detail in a supplementary paper (p. 40).

Experiments were made to determine the length of time necessary to dissolve all of the soluble arsenic from lead arsenates, with the following results:

Determination of soluble arsenic, varying the time of extraction.

Sample.	Time of standing.					
	2 days.	4 days.	6 days.	8 days.	10 days.	16 days.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
A	3.52	3.40	3.52	3.68	3.68	.....
B	1.16	.64	1.04	.80	.92	.....
C	2.76	4.04	4.44	6.28	5.36	.....
D	3.12	3.40	3.80	4.32	3.52	.....
E	.28	.22	.....	.28	.28	0.22
F	.56	.56	.....	.....	.56	.....
G	.17	.17	.17	.17	.17	.17
H	5.54	6.28	6.08	5.88	6.36	6.50

From these results it appears that the time for extraction could be reduced to from two to four days, and this point should be further investigated next year for the purpose of determining more definitely the best period to be adopted for this extraction. The referee also recommends that the method for "Preparation of sample" and "Moisture" (Bulletin 107, Revised, p. 239) be changed to read as follows, and that the methods here outlined for the determination of free acetic acid and for free ammonia be made provisional:

(*a*) Preparation of Sample.

In case the sample is in the form of a paste mix it thoroughly and remove therefrom a sufficient amount to make a quantitative determination of free acetic acid or ammonia, if either is present; transfer this portion to a bottle and stopper tightly until ready for its analysis. Dry the whole of the remainder, if a pound or less, at from 80° to 100° C. until dry enough to powder readily, without sticking, and obtain loss in weight. If the original sample is larger than 1 pound, mix the whole thoroughly, remove therefrom a representative sample of about 1 pound and proceed as directed above. Powder the sample thus obtained and determine the remainder of the volatile matter as follows:

(*b*) Moisture.

Dry 2 grams of the powdered sample (prepared as above if not already dry enough to powder) in an air oven at 105° to 110° C. to constant weight. Calculate the total volatile matter from this loss and the loss obtained in the preliminary drying. Subtract from this total volatile matter any free acetic acid or free ammonia that may be present in the sample and report the remainder as moisture.

(*c*) Free Acetic Acid.

Weigh out from 2 to 10 grams of the original sample, transfer to a flask with from 20 to 40 cc of water, connect with a condenser, and heat to boiling. Pass steam through the solution, regulating the flame under the flask so that the volume will remain nearly constant, and collect about 200 cc of distillate. Titrate the distillate with tenth-normal sodium hydroxid, using phenolphthalein as indicator, and calculate as acetic acid.

(*d*) Free Ammonia.

Wash from 2 to 10 grams of the original sample into a distillation flask and dilute to about 150 cc. Boil down to about 25 cc and collect the distillate in standard acid. Titrate with standard alkali, using cochineal as indicator, and calculate the ammonia from the acid equivalent.

London Purple.

The work on London purple has been limited to the determination of arsenious and arsenic oxids by Method I (provisional), Bulletin 107, Revised, page 28, and total arsenic oxid, Method II, proposed by the present referee, and published in the proceedings of the twenty-fifth and twenty-sixth annual conventions of the association (Bulletin 122, p. 105; Bulletin 132, p. 42).

Cooperative work on London purple.

Analyst.	Arsenious oxid (As_2O_3).	Arsenic oxid (As_2O_5).	
		Method I.	Method II.
	Per cent.	*Per cent.*	*Per cent.*
R. J. Davidson, Blacksburg, Va	12.87	28.16	29.26
	12.90	28.17	29.34
H. S. Stahl, Blacksburg, Va	12.80	27.96	28.47
	12.94	28.22	28.47
J. W. Calvin, Manhattan, Kans	12.88	29.20	29.08
	12.91	29.46	29.20
	.....	29.11	29.17
H. R. Watkins, Washington, D. C	12.86	.....	[1] 32.93
	12.92	29.77	[1] 32.93
T. E. Keitt, Clemson College, S. C	13.22	29.88	28.74
	13.29	28.88	28.74
	13.22	29.00	28.83
	13.15	29.05	28.88
W. D. Lynch, Washington, D. C	12.91	27.04	29.80
	12.94	27.00	29.70
R. C. Roark, Washington, D. C	13.12	29.50	29.90
	13.19	29.71	29.79
W. B. Pope, Washington, D. C	13.18	28.63	29.65
	13.18	28.72	29.65
C. C. McDonnell, Washington, D. C	12.86	29.71	29.92
	12.89	29.51	29.88
Average	13.01	28.78	29.29

[1] Omitted from average.

J. W. Calvin reports that it is very much easier to obtain good results by Method II, which he considers much more satisfactory than Method I. *Mr. Keitt* states that he was much pleased with Method II because the end reaction was very sharp.

The method for arsenious oxid has given satisfactory results after years of trial, and therefore the referee recommends that it be adopted as official. Method I for total arsenic oxid will give good results if carefully carried out, but it is quite troublesome if one has not had considerable experience with it. Method II is much easier of manipulation and gives more satisfactory results. This is the third year it has been before the association and no one has reported any difficulty with it. The two high results reported in the table are probably due to not having boiled off the nitric acid after destruction of the organic matter.

Cyanids.

It has been found that for fumigation work the determination of chlorin in potassium or sodium cyanids is as necessary, if not more so, as that of cyanogen, and an official method for its determination is therefore desirable; that recommended for trial is the Gatehouse [1] method, which consists in titrating with twentieth-normal silver nitrate solution, using potassium chromate as indicator. The total titration minus twice the titration for cyanogen [2] gives the silver nitrate equivalent of chlorin.

[1] Sutton's Volumetric Analysis, 9th ed., p. 201.

[2] U. S. Dept. Agr., Bureau of Chemistry Bul. 107, Revised, p. 30.

Cooperative results on cyanids.

Analyst.	Cyanogen.	Chlorin.	Analyst.	Cyanogen.	Chlorin.
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
R. J. Davidson, Blacksburg, Va.	34.27	9.43	W. B. Pope, Washington, D. C.	34.21	9.17
	34.26	9.40		34.23	9.22
J. W. Calvin, Manhattan, Kans.	34.08	9.49	R. C. Roark, Washington, D. C.	34.12	9.26
	34.04	9.50			
	34.12	9.45	C. C. McDonnell, Washington, D. C.	34.52	9.29
C. E. Bradley, Corvallis, Oreg.	34.53	9.36		34.55	9.22
	34.58	9.39		34.48	9.18
H. R. Watkins, Washington, D. C.	34.44	9.64			
	34.44	.....	Average.....	34.30	9.43
T. E. Keitt, Clemson College, S. C.	34.16	9.94			
	34.06	9.96			

The results on cyanogen and chlorin are both very good, and the referee recommends that the method for chlorin be adopted as official.

RECOMMENDATIONS.

It is recommended—

(1) That under lead arsenate the methods for Preparation of sample and Moisture be changed to read as outlined on page 38, and adopted in this form as official methods.

(2) That the provisional method for total arsenic oxid in lead arsenate be adopted as official (Bulletin 107, Revised, p. 239).

(This recommendation was approved by the association last year and referred for final action this year.)

(3) That further study be made of methods for the determination of total lead oxid in lead arsenate, particularly the chromate method as proposed by the present referee. (See following paper.)

(4) That the method for soluble arsenic in lead arsenate be further studied as regards the time of standing for the solution of soluble arsenic.

(5) That Method I for total arsenious oxid in London purple (Bulletin 107, Revised, p. 28) be adopted as official.

(6) That Method II as proposed by the referee, Bureau of Chemistry Bulletin 132, page 43, for total arsenic oxid in London purple be adopted as official.

(7) That the Gatehouse method for chlorin in cyanids be adopted as official.

(8) That the provisional cyanid method for formaldehyde be changed to read as follows: Under 2, line 8, page 33, Bulletin 107, Revised, strike out "dilute formaldehyde solution" and insert the words "formaldehyde solution containing not over 2.5 grams of a 1 per cent solution or the equivalent," and that the method as changed be adopted as official. (This recommendation was approved in 1909 and referred to the association for final action.)

DETERMINATION OF LEAD IN LEAD ARSENATE AS LEAD CHROMATE.

By C. C. McDONNELL and R. C. ROARK.

The determination of lead in lead arsenate by the method which has been adopted as provisional by this association (Bulletin 107, Revised, p. 239) has been found to give unsatisfactory results in case there are present certain impurities in the lead arsenate, such as lime or calcium salts. This is due to the fact that the calcium sulphate formed is insoluble in the alcohol used and is therefore weighed with the lead sulphate, thus giving too high results. The method of separation with hydrogen sulphid can be used but this is quite a long and disagreeable operation. In order to obviate all these difficulties the following modification of the chromate method has

been devised and works satisfactorily, giving good results and at the same time requiring only a fraction of the time necessary for the other methods. A complete determination can be made in about three hours, and a series of ten requires but little more time. The usual method of determining lead as the chromate in acetic acid solution can not be used in this case because lead arsenate is insoluble in acetic acid; if, however, only a small excess of nitric acid is present and quite a large amount of chromate is added in excess of the amount required to combine with the lead, the precipitation of the lead is complete. The details of the proposed method are as follows:

Treat 2 grams of the sample with 50 cc of nitric acid (1:4), heat the solution, filter if an insoluble residue remains, wash and make to 200 cc. Pipette 50 cc of this solution into a 400 cc beaker, dilute to at least 300 cc, heat nearly to boiling, add sodium or ammonium hydroxid to incipient precipitation, then dilute nitric acid (1:10) to redissolve the precipitate, avoiding more than a slight excess; then add to this boiling solution 50 cc of a 10 per cent potassium chromate solution and stir thoroughly during the addition. The chromate solution should be nearly boiling and added to the lead solution by means of a pipette delivering 50 cc in about 40 seconds. If the lead chromate is precipitated hot and stirred vigorously during the precipitation it will settle clear in 15 minutes or less, when it is ready to be filtered. Filter while hot, collecting the precipitate in a weighed gooch, and wash with boiling distilled water until the wash water does not show the least tinge of yellow. Dry the precipitate in an air oven at from 140° to 150° C. to constant weight. From the weight of lead chromate obtained, calculate the per cent of lead monoxid. In preparing the filter the asbestos mat should be thick and pressed down firmly, then washed and dried at from 140° to 150° C. The Gooch crucibles should be cooled in a desiccator over sulphuric acid as they take up a little moisture over calcium chlorid.

This method would not be applicable in the presence of silver, bismuth, barium, manganese, mercury, or much iron. Iron is the only one of these occurring in commercial lead arsenate and this has never been found in sufficient amounts to interfere with the method. The method has been tried on nitrate, acetate, and arsenate of lead and on various mixtures of these with calcium salts and the results given in the following tables obtained. In working with lead salts soluble in water, such as lead nitrate or acetate a slight excess of nitric acid should be added before adding the chromate solution.

Determinations of lead by two methods as applied to nitrates and acetates.

Material.	Chromate method (PbO).	Converted into lead sulphate and weighed as lead oxid.
	Per cent.	*Per cent.*
Lead nitrate c. p. (theory for lead monoxid 67.38 per cent)	67.35	67.29
	67.25	67.33
	67.30	67.42
	67.43	.....
Lead nitrate, c. p. to which was added ½ part calcium arsenate	67.20	.....
	67.19	.....
	67.33	.....
Lead nitrate to which was added 1½ parts calcium arsenate	67.30	.....
	67.60	.....
Lead nitrate plus 1 part calcium oxid	67.28	.....
Lead nitrate plus 5 parts calcium oxid	67.27	.....
Lead acetate c. p. cryst. (partially dehydrated)	60.90	60.81
	60.87	61.01
	.....	60.94
	.....	60.80
	.....	60.84
Lead acetate plus 5 parts calcium oxid	61.03	.....

Determinations of lead in lead arsenate by the chromate and provisional methods.

Sample.	Chromate method (PbO).			Provisional method (PbO), nothing added.
	Nothing added.	1 part calcium oxid added.	5 parts calcium oxid added.	
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
A.....	74.09	74.01	73.90	73.21
	74.02	74.10	74.08	72.97
	73.94	.....	.....	.....
B.....	70.61	70.47	70.36	70.14
	70.57	.....	.....	.....
C.....	64.77	64.81	64.60	64.13
	64.70	.....	.....	.....
D.....	67.45	67.37	67.39	66.32
	67.25	.....	.....	.....
E.....	61.34	61.50	61.44	60.60
	61.26	.....	.....	.....
F.....	60.31	60.49	60.32	59.54
	60.28	.....	.....	.....
G.....	70.91	71.09	71.14	69.40
	70.98	.....	.....	.....
H.....	71.20	71.27	71.29	69.48
	71.34	.....	.....	.....
I.....	59.73	.....	.....	.....
	59.67	59.84	59.67	[1] 59.45
	59.74	60.05	59.91	[1] 59.40
	60.08	.....	.....	[1] 59.75
	59.87	.....	.....	[1] 59.53
	59.80	.....	.....	.....
	60.03	.....	.....	.....
	60.11	.....	.....	.....
J.....	69.11	.....	.....	69.26
	69.05	.....	.....	69.18

[1] Precipitated as sulphid and weighed as sulphate.

From these results it will be seen that when working with lead arsenate the lead oxid found by the chromate method averages about 0.75 per cent higher than by the provisional method. The tendency of the provisional method is always to give slightly low results on pure lead arsenate and those obtained by the chromate method probably more nearly represent the correct amount present. In the presence of lime, even to the extent of five times the weight of the sample, that is 2.5 grams of calcium oxid to 0.5 gram of lead arsenate, the same results were obtained as when no lime was present, in practically all cases. In such samples the sulphate method would be entirely unreliable. From the work done with this method the authors are of the opinion that it will be found reliable for the determination of lead in commercial lead arsenates and its further trial is recommended.

REPORT ON WATERS.

By J. K. Haywood, *Referee*, and W. W. Skinner, *Associate Referee*.

The work on waters for this year has been restricted to the study of mineral-water analysis, although methods for other groups of waters were offered for consideration in 1909, inasmuch as it seemed probable that more work than this could not be performed by the station chemists. On June 22 a letter of instructions was sent to the 13 chemists who had offered to collaborate, together with Circular 52 containing the methods to be tested. This letter read in part as follows:

Please make the following determinations as given in this circular: Nitric acid, page 4; free ammonia, page 5; chlorin, total salts in solution, loss on ignition, silica, iron, aluminum, and manganese on page 6; calcium, magnesium, sulphuric acid, potassium, sodium, and lithium on page 7, and carbonic and bicarbonic acids on page 11. I am also inclosing one of our regular report cards used in the Water Laboratory of this bureau

upon which it is desirable to have your results submitted, as it will materially facilitate the collating and digesting of the several reports.

The water is rather highly mineralized and should be examined as soon after you receive it as possible. The nitric acid, free ammonia, chlorin, carbonic, and bicarbonic acids at least should be determined at your earliest convenience. Then if for any reason the work must be delayed portions may be withdrawn, acidified with hydrochloric acid, and put aside for future work. One liter in duplicate should be used for the determination of silica, iron, and aluminum, calcium, and magnesium. One liter in duplicate should be used for sulphuric acid, potassium, sodium, and lithium. This will consume 4 liters of the water and will give about 4 liters for the remainder of the analysis and such repeating as may be deemed necessary. If you vary the technique in any particular from that described in Circular 52, will you kindly note same fully in your report, giving in detail reasons for same. I shall appreciate it if the coworkers on this important subject will let me have their final results not later than September 1.

Results have been received from eight of the collaborators. The methods tested have been studied for the past 10 years by both the referee and the associate referee, and have been carefully compared with various other methods of analysis. Also, eight or ten men, working under the direction of the writers, have compared these methods for several years past. The total work has indicated that the methods are extremely accurate and that various analysts can obtain results which compare very favorably with each other.

In making up the sample for cooperative work, filtered Potomac River water, of which various analyses have been made by a number of chemists, served as the basis. To this were added known quantities of different salts. Through certain unforeseen reactions a certain amount of precipitation of carbonates took place. These were nearly all brought into solution by a small amount of sulphuric acid, and the resulting solution with a very small amount of residue was filtered. An artificial water was thus made in which the amount of the various ions was approximately although not exactly known. Enough was known about the composition of the water thus prepared, however, to be sure that the subsequent analysis of it made in the Bureau of Chemistry and numbered "one" in the accompanying table corresponded closely to the amounts of the various ions present. Following are the results obtained by various analysts:

Analyses of water.

[Expressed as ions in parts per million.]

Analysts.	Silica (SiO_2).	Sulphuric acid (SO_4).	Bicarbonic acid (HCO_3).	Nitric acid (NO_3).	Chlorin (Cl).	Iron (Fe).	Aluminum (Al).	Manganese (Mn).	Calcium (Ca).	Magnesium (Mg).	Potassium (K).	Sodium (Na).	Lithium (Li).	Ammonium (NH_4).
Number 1....	4.90	219.10	286.60	1.50	48.00	0.3		None.	107.10	32.00	7.20	54.80	0.70	Tr.
Number 2....	2.82	223.75	309.57	44.160	1,135.00	1.32	0.49	None.	110.30	41.20	16.80	110.30	11.30	10.340
Number 3....	4.45	219.85	281.50	2.520	49.75	0.33		Tr.	108.25	31.05	6.55	55.90	.67	.088
Number 4[1]...	5.00	216.33	271.45	42.240	49.70	2.19	.65	None.	108.65	30.98	6.71	54.75	.83	.119
Number 5[2]...	6.30	211.90	.....	1.990	52.00	1.19		0.94	116.51	39.59	6.88	56.46	1.07	.069
Number 6[3]...	6.03	237.60	274.50	1.100	53.10	3.94	None.	None.	104.10	22.34	4.72	35.66	.65	.128
Number 7....	6.60	223.60	271.45	.017	45.75	1.33		None.	109.90	33.60	5.60	40.20	.64	.089
Number 8....	3.10	220.10	302.00	1.000	57.10	9.80	.....	.....	119.00	41.20	4.60	42.50	.....	1.1

[1] After silica has been determined by volatilization with sulphuric acid and hydrofluoric acid, the residue of iron and aluminum should be dissolved in hydrochloric acid and the solution added to the filtrate from the digestion of the insoluble residue first obtained before that filtrate is made up to definite volume. Again, in the determination of potassium and lithium a correction factor is used. It occurs to me that in the case of potassium particularly the correction factor should be somewhat dependent upon the particular aliquot portion used.

[2] In the evaporation of the original sample for silica determination a porcelain instead of a platinum dish was used.

[3] We evaporated the water in porcelain dishes instead of platinum. Iron was determined from an aliquot by the Zimmerman-Reinhardt method. Lime was determined by the same permanganate solution that was used for the iron. We use these methods for iron and lime because we have found them more rapid and quite as accurate.

The results of this year's work when the entire report of one analyst is compared with that of another are somewhat disappointing and indicate that further and more careful comparative work on the part of the analyst will have to be performed before the methods are adopted as official. Only two sets of results (Nos. 1 and 3) correspond to each other closely throughout the entire analysis. However, when individual determinations are considered, the outlook is more encouraging and shows that in most of the individual determinations the majority of the analysts were able to obtain results which agree fairly well.

For silica results, analysts 1, 3, and 4 agree most satisfactorily, while analysts 1, 3, 4, and 6 agree only fairly well. Analysts 5 and 7 are evidently slightly high, while analysts 2 and 8 appear to be low. It is probable that the low results in these determinations are due to insufficient drying of the residue or to excessive heating of the residue from the hydrochloric-acid extraction, while high results are due to insufficient washing of the silicic-acid residue.

For sulphuric-acid ion, analysts 1, 3, and 8 are in close agreement, while all the analysts except No. 5 and No. 6 agree quite closely. Analyst No. 5 is seen to be slightly low, while analyst No. 6 appears to be slightly high. Just why one of these analysts should have obtained low results and the other high results can not be explained.

For bicarbonic-acid ion a very close agreement between different analysts could hardly be expected, as the amount of this constituent varies to a slight extent according to the period that elapses between the preparation of the sample and the analysis and the temperature at which the sample has been kept. To make a close comparison of the work of different analysts on this determination it would be necessary to have several analysts examine a sample under identical conditions. On the whole, the agreement between analysts 1, 3, 4, 6, and 7 is fairly satisfactory, while analysts 2 and 8 appear to have obtained high results.

For the nitric-acid ion the results are very unsatisfactory. While analysts 1, 5, 6, and 8 obtained results agreeing fairly well, they are not so near together as they should be. The results of analyst 3 appear to be slightly high, those of analyst 7 quite low, while the figures reported by analysts 2 and 4 are simply inexplicable. Probably some of the analysts did not add an amount of chlorid to the standards corresponding to the amount of chlorid in the water; but this would not explain the extremely high results obtained by analysts 2 and 4 nor the extremely low figures given by analyst 7.

The results for chlorin are very unsatisfactory. The determination made by analyst 2 can at once be eliminated as impossible, and for as basic a determination as chlorin the results of the other analysts vary too much one from another. Since the method used for chlorin is a well-known one which has often been shown to be extremely accurate, it is probable that the variation in this determination is due to the analysts rather than to the method.

There is but little doubt that the results obtained by analysts 1 and 3 for combined iron and aluminum are approximately correct since the amount of these constituents in filtered Potomac water as determined by various analysts at different times has been shown to be from 0.3 to 0.5 part per million. The high results obtained by most of the analysts are probably due either to a slight precipitation of magnesium (because of a deficiency of ammonium chlorid in the solution) or to an incomplete washing of the iron and aluminum hydroxid precipitate.

The results for manganese are very satisfactory with one exception, in which case inexplicably high results were obtained.

For as fundamental a determination as calcium closely agreeing results would be expected. The results of analysts 1, 3, and 4 agree with each other very well, and there is a fair agreement between the reports of analysts 1, 2, 3, 4, and 7. The figures given by analysts 5 and 8 are evidently too high, while those of analyst No. 6 are

evidently too low. There does not appear to be any chemical explanation of the variable results obtained by the different analysts.

In the determination of magnesium, the results obtained by analysts 1, 3, 4, and 7 agree with each other as well as could be expected; those of analysts 2, 5, and 8 also agree with each other fairly well, but are considerably above the results obtained by analysts 1, 3, 4, and 7. From our knowledge of the composition of Potomac water and of the amount of magnesium salts added to it, the actual amount of magnesium present in this sample, by calculation, is in the neighborhood of 30 parts per million. The result obtained by analyst 6 on this sample is evidently too low. There does not appear to be any adequate explanation of the high results obtained in this determination, unless the sodium phosphate was not completely washed out of the precipitate.

The results obtained on potassium by analysts 1, 3, 4, and 5 agree with each other very satisfactorily, analysts 6, 7, and 8 appear to have obtained slightly low figures, while analyst 2 obtained a result which is evidently extremely high. No satisfactory chemical explanation can be offered for the variable results obtained for this determination.

In the sodium determination the data obtained by analysts 1, 3, 4, and 5 agree very satisfactorily. The result obtained by analyst 2 is evidently too high, while those reported by analysts 6, 7, and 8 appear to be low. Since the same analysts obtained low results for sodium and for potassium, it is probable that this was due either to too high heating of the combined chlorids or to incomplete washing of the barium and calcium precipitate. The high results obtained by analyst 2 may be due to incomplete removal of calcium, barium, and magnesium.

The reports made by the various analysts for lithium are very satisfactory with one exception. The high figures in this case are probably due to the incomplete removal of magnesium.

The results obtained for ammonium are very unsatisfactory, and there does not appear to be any adequate explanation of the variation reported, unless the small amount of organic matter present in Potomac water was gradually oxidized and the albuminoid ammonia thus changed to free ammonia. Even then the figures obtained by analysts 2 and 8 would not be explained.

A careful consideration of the tabulated data shows that in nearly every case for individual determinations four or five of the eight analysts were able to obtain concordant results, which from the knowledge of the approximate composition of the water sample used are known to be approximately correct. In addition to this, practically all the methods used are standard, well-known methods which have been tested and found to be correct by many different chemists, as well as those in the laboratory of the referees. It would therefore appear that the variation in the results for this year is more a matter of men than methods, and that, with increased familiarity with the methods, much more concordant results will be obtained next year.

As a result of this year's work, it is respectfully recommended that the methods of water analysis tested this year be again tested next year, special attention being given by analysts to following the methods exactly as outlined.

The discussion further emphasized the point that the discrepancies in the results were due to unfamiliarity with the methods and a failure to follow the directions closely, both the internal evidence contained in the report and the experience of others with the procedures involved pointing to this conclusion. Mr. H. E. Patton also called attention to the ion nomenclature employed, stating that in his opinion its use was not theoretically correct, and that the association should revert to the use of the terms employed before the ionic theory was advanced.

REPORT OF COMMITTEE A ON RECOMMENDATIONS OF REFEREES.

By J. K. Haywood, *Chairman*.

(Nitrogen, potash, phosphoric acid, soils, inorganic plant constituents, insecticides, and water.)

Nitrogen.

It is recommended—

(1) That the next referee on nitrogen be requested to study laboratory methods for the determination of the availability of organic nitrogen.

Adopted.

Potash.

It is recommended—

(1) That a study be made of the volumetric and gravimetric cobalti-nitrite methods for another year.

Adopted.

(2) That a further trial be made of the modification of the official method by washing a weighed amount of the sample through filter paper with hot water and determining potash in the filtrate.

Adopted.

Soils.

It is recommended—

(1) That the referee on soils for 1911 be instructed to investigate the subject of a more accurate method for humus determinations.

Adopted.

(2) That the modified cobalti-nitrite method for total potash in soils be further studied.

Adopted as reported by the committee. (Referee recommended adoption as an optional official method.)

(3) That the study of methods for the quantitative estimation of soil acidity be continued.

Adopted.

Mr. Shedd's recommendation that the official method for manganese in soils as given on page 15 of Bulletin 107, Revised, be reworded to read as follows, was referred to Committee A.

Concentrate solution B to about 50 cc, cool, add bromin water until the solution is colored, make alkaline with ammonium hydroxid, and heat to boiling in a covered beaker * * *.

The change insures an ammoniacal solution during boiling which is necessary to bring down manganese, and as only a correction in wording is involved, which does not constitute any alteration in the method, the chairman of the revision committee authorizes the insertion of the suggested reading.

Inorganic Plant Constituents.

It is recommended—

(1) That the peroxid method for sulphur in plants be made official.

Adopted.

(2) That the work on the determination of ferric and aluminic oxids be continued another year.

Adopted. (This recommendation as received from the committee replaced the two made by the referee to the effect that the method for ferric and aluminic oxids be made provisional and that another method be sought for these determinations and that cooperative work be done on a synthetic ash solution if such a method be found.)

Insecticides.

It is recommended—

(1) That the provisional method for total arsenic oxid in lead arsenate be adopted as official.

Adopted, having been referred from the previous year for final action.

(2) That a further study be made of methods for the determination of total lead oxid in lead arsenate, particularly the chromate method as proposed by the present referee.

Adopted.

(3) That the method for soluble arsenic in lead arsenate be further studied as regards time of standing for the solution of soluble arsenic.

Adopted.

(4) That Method I for total arsenious oxid in London purple as given in Bulletin 107, Revised, page 28, be adopted as official.

Recommendation adopted and referred to the association for final action in 1911.

(5) That Method III as proposed by the referee in 1909 (see Bulletin 132, p. 43) for total arsenic oxid in London purple be adopted as official and designated as Method II.

Recommendation adopted and referred to the association for final action in 1911.

(6) That the Gatehouse method[1] for the determination of chlorin in cyanids be adopted as official.

Recommendation adopted and referred to the association for final action in 1911.

(7) That the provisional method for the analysis of lead arsenate (Bulletin 107, Revised, p. 239) be changed as follows:

For paragraphs (*a*) and (*b*) on "Preparation of sample" and on "Moisture," respectively, substitute sections suggested in referee's report, and add methods proposed for the determination of free acetic acid and of free ammonia.

These additions and changes were all adopted as provisional.

(8) That the provisional cyanid method for formaldehyde be changed to read as follows: Under (*b*) (2) line 8, page 33, Bulletin 107, Revised, strike out "dilute formaldehyde solution" and insert the words "formaldehyde solution containing not over 2.5 grams of a 1 per cent solution or the equivalent," and that the method as changed be adopted as official.

This recommendation was made in 1909 and came up for final action. The committee recommended that the referee on insecticides so change the method as to provide for neutralizing the acidity of the peroxid before using it as a reagent, and that the method, with this change incorporated, be adopted as official.

Adopted.

(In accordance with the action of the committee the referee submits the following statement to replace the data under "(1) Solutions required," page 33, Bulletin 107, Revised:

(*a*) *Sulphuric acid*, a normal solution.
(*b*) *Sodium hydroxid*, a normal solution.
(*c*) *Hydrogen dioxid*, an approximately 3 per cent solution. (In case the hydrogen dioxid solution is acid it should be neutralized with normal sodium hydroxid, using litmus solution as indicator.)
(*d*) *Indicator*, a solution of purified litmus.

Waters.

It is recommended—

(1) That the methods for the analysis of waters submitted in 1909, and printed in Circular 52, page 4, be again tested by the association, paying special attention to following the details of the methods as outlined.

Adopted.

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[1] Sutton's Volumetric Analysis, 9th ed., 1904, p. 201; Bureau of Chemistry Circular 10, Revised, p. 6.

No report was made by the committee on the availability of phosphoric acid in basic slag, and by vote of the association the committee was continued, the incoming president to take any action necessary in regard to the personnel of the committee.

No formal report was made by the committee on food standards, the chairman, Mr. Frear, making a verbal statement of progress, in which he said that the committee had been especially considering standards for condensed milks and compressed yeast. Mr. Frear also stated that the committee would be glad to have suggestions from the members of the association in regard to points calling for special study, the fixing of chemical and physical limits for constituents not now included in the standards as adopted, such as suggesting refractive limits for milk serum, definitions for milk chocolates, etc.

This report of progress was received by the association and the committee continued.

REPORT OF COMMITTEE ON UNIFICATION OF TERMS.

Mr. Davidson, chairman of the committee, made the following statement:

The question of the unification of terms for reporting analytical results in soils, fertilizers, and ash having been before the Association of Official Agricultural Chemists for several years, it was finally decided, by the following resolution adopted at the meeting of 1907, that the subject be brought to the attention of the International Congress of Applied Chemistry:

That the suggestion of the committee looking toward the ultimate adoption of the element system be approved, but that no State should discontinue the use of the terms now in use until such discontinuation is also approved by this association and that meanwhile the subject should be brought before the International Congress of Applied Chemistry in an effort to secure international agreement.

The report sent to the Seventh International Congress of Applied Chemistry did not reach London in time to be given a place on the program and the committee proposes to communicate with the secretary of the eighth international congress and request that the executive committee of that congress be asked to make provision for the full consideration of the matter. No argument will be presented by the committee in favor of any specific action, but the whole subject will be presented for the action of the congress.

The report was accepted and the committee continued.

REPORT OF COMMITTEE ON STANDARDIZATION OF ALCOHOL TABLES.

At the last meeting of the association the committee on the standardization of alcohol tables was continued, in order that they might have opportunity to consult with the revision committee of the Pharmacopœia in order to insure, if possible, final action which would be uniform.

There appears to be one fundamental question which must be settled before any step in advance can be taken, and that is whether the temperature of 60° F. shall be accepted as the standard. In this connection certain evidence has been collected which seems to have a direct bearing on this case. Section 3249 of the Revised Statutes of the United States states: "Proof spirit shall be held to be that alcoholic

liquor which contains one-half its volume of alcohol of a specific gravity of seven thousand nine hundred and thirty-nine ten-thousandths at 60° F.," upon which all of the tests of the Bureau of Internal Revenue are based. Section 3250 of the Revised Statutes states: "In all sales of spirits a gallon shall be held to be a gallon of proof spirit, according to the standard prescribed in the preceding section set forth and declared for the inspection and gauging of spirits throughout the United States." It therefore is plain that the buying and selling of alcohol must be based on volume percentage at 60° F. until such time as Congressional action may change this temperature. This means that the Internal Revenue Service and all other chemists who have to deal with alcohol buying and selling will be compelled to use a volume percentage at 60° F.

In addition to the fact that 60° F. is the standard in this country, it is also the standard in practically every country in the world for alcohol; and as alcohol is almost universally taxed, the laws of these countries have taken into consideration the temperature of determination, so that any change in temperature for alcohol determinations is practically impossible.

The pharmacopœial committee has prepared a table for alcohol by volume at $\frac{25° \text{ C.}}{25° \text{ C.}}$, but such a table can have only a very limited use, and there seems to be no reason for making this change. The Bureau of Standards, however, has prepared a series of tables varying from 15° C. to 25° C., giving the absolute density of mixtures by weight of ethyl alcohol and water, and also a table for converting density at 20° C. in 0.1 per cents by weight. A table for the conversion of percentages by weight into the corresponding percentages by volume at 60° F. is also given, thus facilitating a ready conversion of these data and enabling one to use the temperature at 25° C. for the actual determination of per cents by weight of alcohol in mixtures, and by a very simple table converting this into the standard—that is, the per cent of alcohol by volume at 60° F. It would therefore seem that as far as the evidence now available is concerned, we must adopt the standard of reporting alcohol by volume at 60° F. By the use of the table of the Bureau of Standards the actual determination of alcohol can be made at 25° C. and later accurately converted into per cents by volume at 60° F.

The committee therefore recommends that the association adopt provisionally the table of the Bureau of Standards as published in Circular 52 of the Bureau of Chemistry, and also that the committee on this subject be continued in order that they may take up the matter further with the revision committee of the Pharmacopœia.

L. M. Tolman, *Chairman.*
M. E. Jaffa.
A. B. Adams.
R. J. Davidson.
H. E. Barnard.

The report was adopted and the committee continued.

Mr. Tolman, as chairman of the committee on the unification of methods of analysis of fats and oils, stated that only a report of progress could be made; that some work had been done in this country, but more time was necessary to secure international cooperation, and it was the hope of the committee that by another year, in collaboration with the American Chemical Society and the American Society for Testing Materials, an international committee would be appointed.

The report was received and the committee continued.

Mr. Bigelow, as chairman of the committee on the compilation of by-laws, made a partial report and the matter was referred back to the committee for conference with the committee on amendments to the constitution.

REPORT OF COMMITTEE ON THE TESTING OF CHEMICAL REAGENTS.

By L. F. Kebler, *Chairman.*[1]

At the last annual meeting of the association, the committee was instructed to make an inquiry into the nomenclature most suitable for use in conjunction with chemical reagents, and report at this meeting. The chairman has given this subject careful consideration for a number of years. He has discussed it with analytical, theoretical, and manufacturing chemists, and virtually all are of the belief that the present terms used in designating chemical reagents are wanting in definiteness. This fact is also impressed on us by looking over the various chemical catalogues, or reading contributions to chemical literature and discussions of analytical methods.

The time-honored and much-abused designation "C. P." has been rapidly losing ground. Some manufacturers have dropped it entirely, others retain it, and properly, in connection with certain chemicals that are in fact chemically pure, and some few still make liberal use of it without any good reason. This designation possibly serves one good purpose, and that is when an order is placed for a chemically pure chemical, and it is found on examination to be contaminated with substances detrimental to analytical work or chemical investigations, it can be rejected unceremoniously. Such a procedure may be a little hard on the manufacturer, but it is only what he deserves for misrepresenting a chemical.

On reading some statements of analytical methods such terms as "hydrochloric acid," "pure hydrochloric acid," "concentrated hydrochloric acid," and "C. P. hydrochloric acid" will be found, all of which may mean one and the same product or different grades of the article. While reviewing a monograph on ethyl ether, the chairman met the names "ether," "pure ether," "specially purified ether," "anæsthetic ether," and "commercial ether." From the context it was difficult, if not impossible, to conclude what was meant. In fact the term "ether" unqualified was applied to a product of about the same purity as that designated "specially purified ether." The terms "anæsthetic ether" and "commercial ether" are sometimes used synonymously, though it is well known that some anæsthetic ether is of a high degree of purity.

Examples of this character could be multiplied indefinitely, but it is not considered necessary to do so in this report. Various efforts have been made to remedy these difficulties, but thus far without success. In view of the conditions at present obtaining the committee has decided to make the following tentative recommendations, so as to bring the subject definitely before the association for discussion. These recommendations provide chemical reagents for all kinds of chemical work at a price commensurate with the importance of the work to be undertaken.

The recommendations are:

(1) That the designation "C. P." be applied only to such chemical reagents as are free from recognizable impurities.

(2) (*a*) That the term "reagent" be applied to all commonly employed chemical reagents which are free from all impurities to such an extent as to permit their use in

[1] In the absence of the chairman the report was presented by Mr. Kilgore.

all ordinary qualitative and quantitative chemical analyses. (*b*) That a specific set of tests, with which the chemical must comply, be drawn up and adopted for each chemical reagent.

(3) That the term "special reagent" be employed only for certain reagents to be used chiefly for making special determinations which require absolute freedom from certain impurities.

The report was adopted and the committee continued.

The association adjourned for the day.

SECOND DAY.

FRIDAY—MORNING SESSION.

The Secretary of Agriculture addressed the association, emphasizing the importance of the chemist's work, especially with reference to work under the food law and the cooperation between the States and the Federal Government in carrying out its provisions.

REPORT ON COLORS.

By W. E. Mathewson, *Associate Referee.*

Cooperative Work.

The cooperative work on colors this year has comprised, first, the securing of a number of dyes of known constitution and purity with which a set of colored food products were made; second, the examination of these and a discussion of the methods by the chemists taking part, and, third, an attempt by the referee to devise a method for the identification of the oil-soluble colors, especially when used in admixture with one another.

Because of confusion in the naming of dyes and the difficulty of obtaining pure samples in commerce many conflicting statements are found in the tables given in the literature; furthermore, probably most of the coal-tar colors used in the manufacture of foods are mixtures of dyes, and any satisfactory method for their identification must provide for some sort of separation of the colors. With these facts in mind, the following set of colored food products was prepared:

Food product.	Color.
1. Jelly	Chrysoidin.
2. Jelly	Orange II.
3. Jelly	Orange I.
4. Jelly	Ponceau 3 R. + Naphthol yellow S.
5. Jelly	Erythrosin. + Ponceau 3 R.
6. Jelly	Naphthol green B.
6a. Liqueur	Do.
7. Jelly	Amaranth. + Naphthol yellow S. + Indigo carmine.
8. Salad oil	Sudan I.

The following data are given regarding the colors used:

Chrysoidin: Made from c. p. materials and recrystallized from alcohol.

Orange II: Made from c. p. material and recrystallized.

Orange I: Certified color; on reduction yielding practically no amino naphthol capable of coupling with diazotized sulphanilic acid to form a red dye (freedom from Orange II), sulphur 9.05 per cent, sodium 6.63 per cent, theory 9.15 per cent, 6.58 per cent.

Ponceau 3 R: Certified color yielding pseudocumidin on reduction; sulphur 12.95 per cent, sodium 9.31 per cent, theory 12.97 per cent, 9.32 per cent.

Naphthol yellow S: Certified color; free from martius yellow, sulphur 8.96 per cent, sodium 12.85 per cent, theory 8.95 per cent, 12.87 per cent.

Erythrosin: Certified color; iodin 55.31 per cent, sodium 5.40 per cent, theory 57.70 per cent, 5.24 per cent.

Naphthol green B: Made from pure materials.

Amaranth: Certified color; sulphur 15.80 per cent, sodium 11.43 per cent, theory 15.91 per cent, 11.44 per cent.

Indigo carmine: Certified color; sulphur 13.42 per cent, sodium 9.64 per cent, theory 13.75 per cent, 9.88 per cent.

Sudan I: Made from c. p. materials and recrystallized from alcohol.

Perhaps because of the boric acid used as a preservative the color of sample 7 changed from brown to bright orange after a few weeks, and tests showed that the indigo carmine had entirely disappeared. The results obtained by the collaborators are given below:

Cooperative results on the referee's samples.

Analyst.	Sample 1.	Sample 2.	Sample 3.	Sample 4.
W. A. Bender, New York	Not identified	Orange II.	Orange I.	Ponceau 3 R. Naphthol yellow S.
A. W. Hansen, Chicago	Fast yellow	do	do	Do.
R. C. Kent, Washington	Chrysoidin	do	do	Do.
H. M. Loomis, Seattle	Chrysoidin R	do	do	Brilliant cochineal 2 R. Naphthol yellow S.

Analyst.	Sample 5.	Samples 6 and 6a.	Sample 7.	Sample 8.
W. A. Bender, New York	Ponceau 3 R. Erythrosin	Naphthol green B.	Naphthol yellow S. Amaranth	Sudan I.
A. W. Hansen, Chicago	do	do	do	Butter yellow.
R. C. Kent, Washington	do	do	do	Do.
H. M. Loomis, Seattle	do	do	do	Sudan I.

Chrysoidin as a basic color does not give very satisfactory results by the double dyeing process, although Rota's scheme should lead to its identification. Orange II, a very common and objectionable color, was identified and distinguished from Orange I by all collaborators, although much confusion exists in the literature regarding its reactions. Naphthol green B was also identified in all cases, although it is very easily destroyed by warming in acid solutions.

To separate the color in sample 8 (salad oil), W. A. Bender used glacial acetic acid, the oil passing into solution with the color being afterwards saponified with potash, the soap taken up with water, and shaken out with petroleum ether. From the petroleum ether solution the small amount of dissolved soap was washed out with water. H. M. Loomis used warm 90 per cent alcohol instead of the acetic acid and A. W. Hansen saponified the oil directly.

Regarding the separation of mixtures, Mr. Hansen recommends the fractional stripping of the dyed cloth with dilute ammonium hydroxid as better than the use of several pieces of wool in dyeing. He says: "I think nothing would help more in the identification of colors than to have the solubilities further worked out along the line indicated by Mr. Loomis."

In the examination of products colored with mixtures of sulphonated dyes the procedure most frequently found useful in the New York laboratory, and applied especially by Mr. Seeker to the separation of the seven permitted colors, depends on the greater solubility of the lower sulphonated dyes in amyl alcohol when the latter is shaken with their acid solutions. The mixture is made strongly acid with hydrochloric acid and shaken out with amyl alcohol. The aqueous portion, if still colored, is treated with sufficient alkali to neutralize most of the acid and warmed with a piece of wool. The combined amyl alcohol solution is shaken out with several small

portions of water; finally, if necessary, with dilute sodium hydroxid. In general, the last fractions contain the lower sulphonated colors. The referee believes that an exact knowledge of the distribution ratios of the various acid dyes between amyl alcohol and dilute acid for certain given concentrations of acid in the watery layer would be of great value in dealing with unknown mixtures. Some of the azo colors yield amins on decolorizing their solutions with a little titanium chlorid or stannous chlorid, and after making alkaline these can be shaken out with ether and identified as given below for the oil-soluble colors.

Separation of Oil-Soluble Colors.

The scheme to be described provides for the separation and identification of the colors named in nearly all mixtures with each other. As the colors of a group do not usually show very great differences in solubility or distribution coefficient, an exact separation by fractional shaking out of the solution is of course not possible. With fair amounts of color such as usually can be obtained from food products, however, it is sufficiently accurate for identification purposes. In nearly all cases the procedure can be shortened by testing the ether solutions obtained in the different groups directly, a few drops being evaporated and the color of the residue with concentrated sulphuric acid observed.

SEPARATION OF COLORS IN ETHER SOLUTION.

I. Shake out with 2 per cent ammonium hydroxid.
Ammonia solution colored (yellow).
Neutralize, shake with ether, evaporate ether and add to residue a few drops of alcohol and a little of a solution of stannous chlorid in hydrochloric acid, or better, a solution of titanium chlorid. Make strongly alkaline with sodium or potassium hydroxid, add water to make 15 or 20 cc and distil from a small flask until from 7 to 10 cc are obtained If oil is present, shake the alkaline mixture with ether; shake the latter with dilute hydrochloric acid, add excess of potassium hydroxid to the acid solution and distil. Distillate contains anilin: *Sudan G.*

II. Shake out the ether solution (from which Sudan G has been removed) with 15 per cent hydrochloric acid (1 volume of concentrated hydrochloric acid and 2 volumes of water). If the acid extract is colored, neutralize, take up color with ether and shake out latter solution with 9 per cent hydrochloric acid (1 volume of concentrated hydrochloric acid minus 4 volumes of water).

a. Readily extracted (with violet red color). Dye separated from extract by neutralizing, and shaking with ether gives red color in concentrated sulphuric acid. On reduction and distillation as under Sudan G it yields anilin: *Benzene-azo-α-naphthylamin.*

b. Extracted with difficulty (with red color). Nearly neutralize some of the acid extract, cool to room temperature, add 1 drop of 5 per cent sodium nitrite solution and allow to stand for a few minutes. Pour the mixture into 15 cc of 5 per cent sodium carbonate solution to which has been added a few drops of 1 per cent β-naphthol solution. If a red color (due to formation of Sudan III) is produced, shake the mixture with ether, wash the ether solution, evaporate and test residue with 85 to 90 per cent (volume) of sulphuric acid. Intense green color: *Anilin yellow.*

Reduce another portion of the extract with stannous chlorid, or better, titanium chlorid. Add excess caustic alkali and shake with ether. Wash ether solution with water, then shake it with from 5 to 8 cc of dilute fifth-normal hydrochloric acid. Draw off acid solution and add to it a drop or two of 0.2 per cent ferric chlorid solution. Intense rose color changing to blue: *Butter Yellow.*

c. Not extracted. Extracted by 15 per cent hydrochloric acid with violet color. Yields α-naphthylamin on reduction and distillation: *Amino-azo-α-naphthalin.*

III. Shake out ether (from which the preceding colors have been removed) with 5 per cent potassium hydroxid solution.

a. Readily extracted (brownish-red solution). On reduction and distillation yields anilin: *Benzene-azo-α-naphthol* (unsulphonated base of Orange I).

b. Extracted with difficulty (deep red solution).
On reduction and distillation yields α-naphthylamin: *Sudan Brown.*
On reduction yields β-naphthylamin: *β-naphthalin-azo-α-naphthol.*

IV. If the ether solution from which preceding colors have been removed is deeply colored, evaporate, add a little alcohol, reduce with stannous chlorid and hydrochloric acid, make alkaline and distil as under Sudan G.
Yields xylidin: *Sudan II.*
Yields anilin: *Sudan I and Sudan III.* (These dyes form red and green solutions, respectively, in concentrated sulphuric acid. Sudan I is much more soluble in concentrated hydrochloric acid and in alcohol than Sudan III.)
Yields α-naphthylamin: *Carminaph Garnet.* (If Sudan Brown is present it must be completely extracted, which is somewhat difficult.)

IDENTIFICATION OF THE AMINS IN DISTILLATES.

(1) *β-naphthylamin.*—Shake a portion of the distillate with ether and evaporate the ether with a trace of furfurol (conveniently in ether solution also). β-naphthylamin gives an intense purple, α-naphthylamin a yellowish red, and anilin a crimson residue.

(2) *α-naphthylamin.*—Treat a mixture of a few decigrams of sulphanilic acid in about 50 cc of water with 2 drops of concentrated hydrochloric acid and from 2 to 3 drops of 5 per cent sodium nitrite solution (sulphanilic acid must remain in excess). Add some of this solution to a portion of the distillate. If α-naphthylamin is present an intense rose color appears at once. β-naphthylamin gives a much less marked orange color or turbidity; anilin and homologues no coloration. If anilin is substituted for sulphanilic acid in making the test α-naphthylamin gives an intense rose color. β-naphthylamin in the absence of α-naphthylamin a greenish-brown coloration or turbidity.

(3) *Anilin and homologues.*—Allow the mixture of distillate with diazotized sulphanilic acid (see above) to stand ten minutes, then make alkaline with potassium hydroxid and shake with ether which will take up anilin and homologues if present. Wash ether, shake with very dilute hydrochloric acid and treat latter solution with a drop of 5 per cent sodium nitrite solution. Pour the diazo solution into an excess of 5 per cent sodium carbonate, to which have been added a few drops of 10 per cent β-naphthol. A red color or turbidity indicates the presence of anilin or homologues. Make the mixture alkaline with sodium hydroxid, shake with ether and wash ether solution. Pour into a test tube and evaporate off the ether. Add to the residues from 3 to 4 cc of concentrated hydrochloric acid, heat to a boiling point and add 1 drop of concentrated nitric acid to the solution. With the amounts ordinarily present, xylene-azo-β-naphthol (Sudan II) from xylidin gives a clear yellow solution; benzene-azo-β-naphthol (Sudan I) an orange turbidity. The test can of course be applied directly to mixtures of the Sudans to detect Sudan I.

The amin solution may also be tested with lead dioxid and acetic acid (Lauth's test). It should be strongly acid with acetic acid and contain the amin in such dilution that no coloration appears until the mixture has stood some moments. Under these conditions xylidin gives a purple color and anilin a brown passing to red.

Colors of solutions of dyes in concentrated sulphuric acid.

Anilin yellow	Yellow.	Sudan G	Yellowish brown.
Butter yellow	Yellow.	Benzene-azo-α-naphthol	Violet.
Benzene-azo-α-naphthylamin	Orange red.	Sudan brown	Greenish blue.
Amino-azo-α-naphthalin	Blue.	β-naphthalin-azo-α-naphthol	Violet blue.
Sudan I	Cherry red.	Carminaph garnet	Bluish violet.
Sudan II	Violet red.	Sudan III	Green.

Mr. F. K. Cameron called the attention of the association to the meeting of the Eighth International Congress of Applied Chemistry, which is to be held in 1912, meeting for the first time in this country. He urged the active cooperation of the association in securing to agricultural chemistry the place on the program of the meeting that its importance demanded, stating that no other body of men could so well take the matter in hand. The secretary of the association

emphasized further the importance of such action, and the following motion was introduced by Mr. Brinton and unanimously carried:

Resolved, That the incoming president appoint a committee of three or five members to take under consideration the matter of the cooperation of the association in the Eighth International Congress of Applied Chemistry and to confer with other committees having the matter in charge.

REPORT ON FRUIT AND FRUIT PRODUCTS.

By A. W. Blair, *Associate Referee.*

Mr. Gore, who made the report on fruit and fruit products last year, suggested that the work at present required on methods of titrating to determine total acids seemed to be strictly of a research character, and not ready yet for cooperative investigation, and in view of this fact it seemed worth while to undertake some work on methods of moisture determinations. Only three chemists offered to cooperate in the work. The following instructions, together with a sample of pure blackberry jelly, were sent to these.

Four methods were proposed for cooperative work, as follows:

I. Official method (foods and feeding stuffs). Bulletin 107, Revised, page 38. Use 2 to 4 grams of the material.

II. Provisional method (molasses). Bulletin 107, Revised, page 65 (3). Use 2 to 4 grams of the material. Lead shot may be used instead of sand, if desired, though this should be stated in making report.

III. The Lowenstein alcohol method, J. Ind. Eng. Chem., 1909, **1**: 252. Bureau of Chemistry, Bulletin 132, page 152 (e). Dry 2 to 4 grams of the material in a flat-bottom dish containing stirring rod, to facilitate spreading and stirring the material. Add about 15 cc of 95 per cent alcohol (by volume), stir thoroughly and evaporate on steam bath with frequent stirring; then add another portion of 15 cc of the alcohol and evaporate as before. In case the material is difficult to dry, four applications of alcohol may be used or one or two portions of absolute alcohol. Dry on steam bath for 30 minutes and then transfer to water oven and heat to constant weight at the temperature of boiling water.

IV. Vacuum method, over c. p. sulphuric acid without the aid of heat. Bureau of Chemistry, Bulletin 122, pages 219 to 220, and Bulletin 132, page 150.

Should time allow, it is suggested that the moisture be determined in samples of one or more ripe fruits by the four methods. The results obtained would, of course, serve only as a comparison of the four methods in the hands of each analyst.

The fruit should be prepared as for analysis and cut into thin slices or passed through a meat chopper. Use 10 to 20 grams.

Two laboratories only submitted results. These with comments are as follows:

Moisture determinations on fruit and fruit products (A. W. Blair, Gainesville, Fla.).

Sample.	I. Official method.				II. Provisional method.		III. Lowenstein alcohol method.				IV. Vacuum method over c. p. sulphuric acid.	
	Vacuum 70° C.		Vacuum 100° C.				Water oven.		Vacuum.			
	Time.	Per cent.	Time.	Per cent.	Time.	Per cent.	Time.	Per cent.	Time.	Per cent.	Time.	Per cent.
Pure blackberry jelly....	*Hours.* 6	[1]25.28 25.38 25.53	*Hours.* 11	[2]28.43 28.39 28.35	*Hours.* 30	[2]26.86 26.81 26.76	*Hours.* 25	[2]26.46 26.93 26.66	*Hours.* 1	[1]25.67 25.37 25.58	*Hours.* 218	[2]18.26 18.28 18.25
Fresh pineapple (Red Spanish).....	10½	82.10 82.17 81.97		.....	19	[1]82.87 82.86 82.90		.....	8½	81.86 81.94 81.96	120	81.28 81.39 81.34

[1] Asbestos used in bottom of dishes. [2] Lead shot used in bottom of dishes.

Moisture determinations on fruit and fruit products (A. M. Henry, Tallahassee, Fla.).

Sample.	Air-oven method.			Provisional method.			Lowenstein alcohol method.	
	End of 5 hours.	End of 10 hours.	End of 15 hours.	End of 10 hours.[1]	End of 15 hours.	End of 16 hours.	End of 10 hours.	End of 15 hours.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Pure blackberry jelly.	19.85	22.81	23.25	26.81	27.83	27.83	24.86	25.76
	19.60	22.81	23.77	26.78	27.50	27.51	23.74	24.62
	19.73	22.81	23.85	26.88	27.18	27.24	23.15	23.98

[1] At the end of the eleventh hour the average obtained was 28.39, using 5 grams of sand to 1 gram of sample.

The work is not exhaustive enough to be conclusive with reference to any of the methods. The results obtained by vacuum over sulphuric acid are entirely too low, although drying was continued for more than a week. In the case of the other methods an effort was made to dry to constant weight, but this seemed difficult, and in most cases the samples continued to lose weight. With a few exceptions, duplicate determinations agreed fairly well, though the results obtained by the different methods do not agree closely. With fruits and fruit products the vacuum oven will probably give better results than the other methods, but more work should be done before any definite conclusions are drawn.

REPORT ON VINEGAR.

By R. W. Balcom, *Associate Referee.*

Following the suggestions and recommendations made by the associate referee in 1909, the question as to the retention of acetic acid in the determination of the total solids in vinegar has been further investigated this year.

Other investigators having used larger quantities of the sample than 10 cc, the amount specified in the present method of determining solids, it remained to be determined whether the retention of acetic acid and the consequent higher results would be appreciable when only 10 cc were used for this determination. That it is appreciable is shown by the results given in Table 1.

The evaporations on the steam bath previous to drying in the water oven were carried out by using 5 cc portions of water after each evaporation. All weights are given in grams per 100 cc, although in the actual determinations 10 cc of the sample were used.

The table shows, for the 18 samples, an average loss in weight of 0.113 gram. To meet the objection that this loss might be due entirely to volatilization of some constituent other than acetic acid or to increased decomposition of the sugars present, the residues were dissolved in water and titrated with tenth-normal sodium hydroxid. Assuming that the difference in the amounts of alkali used for the titrations represented acetic acid which was driven off by the repeated evaporations, the actual weight of acid so expelled was calculated and is given in the last column of the table. The average amount for the 18 determinations is 0.059 grams, or approximately one-half of the total loss in weight.

Four evaporations were carried out, as is indicated in the table. Windisch and Schmidt[1] determined the volatile acid driven off after each evaporation by distilling the residues with steam and titrating the distillate. They found that three evaporations were necessary to completely expel the acid, but were working on wine vinegars, in which the total solids averaged less than are usually found in cider vinegars. Fröhner[2] and Köpfe[3] recommend two evaporations, while Russell and Hodgson[4], working

[1] Deut. Essigindustrie, 1908, **12**: 257; Zts. Nahr. Genussm., 1908, **15**: 269-72; Chem. Abs., 1909, **3**: 810.
[2] Zts. Nahr. Genussm., 1905, **9**: 361-3.
[3] Pharm. Zentralhalle, 1905, **46**: 84.
[4] Analyst, 1910, **35**: 346-8.

on malt vinegars and using 100 cc of the sample in each case, found that three evaporations were necessary to expel the acid completely. The results in Table 1 were obtained by the associate referee.

TABLE 1.—*Amounts of acetic acid expelled by repeated evaporations.*

Sample No.	Solids.			Tenth-normal sodium hydroxid.		
	One evaporation.	Four evaporations.	Difference.	Used after one evaporation.	Used after four evaporations.	Difference expressed as acetic acid.
				cc.	*cc.*	*Grams.*
1	2.710	2.665	−0.045	18.4	12.8	0.034
2	2.341	2.327	− .014	11.4	6.7	.028
3	2.565	2.566	+ .001	19.5	12.4	.043
4	2.304	1.951	− .353	55.6	3.2	.314
5	3.408	3.325	− .083	45.5	39.7	.035
6	2.057	1.975	− .082	13.5	9.0	.027
7	3.209	2.609	− .600	75.5	18.0	.345
8	3.033	2.950	− .083	29.8	24.5	.032
9	3.096	2.920	− .174	67.7	55.7	.072
10	3.468	3.419	− .049	14.2	12.6	.010
11	2.482	2.446	− .036	13.7	13.0	.004
12	1.942	1.875	− .067	9.0	6.5	.015
13	2.970	2.885	− .085	13.5	10.0	.021
14	3.000	2.940	− .060	12.8	10.3	.015
15	2.735	2.695	− .040	16.5	15.0	.009
16	2.220	2.135	− .085	14.4	11.3	.019
17	2.905	2.800	− .105	19.8	15.9	.023
18	2.640	2.570	− .070	14.5	10.8	.022
Average			− .113			.059

Mr. E. G. Grab, working upon six samples of cider vinegar procured in Nashville, obtained the results given in Table 2. These figures show that the loss in weight is greatest between the first and second evaporations, which fact is confirmed by other investigators. On five of the six samples the amount of tenth-normal alkali required to neutralize the acidity of the residues after the first, second, third, and fourth evaporations was determined, 100 cc of the vinegar being used in each case. These results are also given in Table 2.

TABLE 2.—*Experiments on loss in weight during evaporation (E. G. Grab).*

SOLIDS (GRAMS PER 100 CC).

Number of evaporations.	Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 4.	Sample No. 5.	Sample No. 6.
Using 10 cc of sample:						
1	2.66	2.00	2.41	2.59	3.49	2.28
2	2.53	1.91	2.25	2.46	3.29	2.16
3	2.50	1.89	2.20	2.41	3.25	2.12
Using 25 cc of sample:						
1	2.72	2.08	2.53	2.67	3.57	2.34
2	2.55	1.91	2.28	2.51	3.37	2.22
3	2.57	1.93	2.26	2.49	3.34	2.19

TENTH-NORMAL ALKALI REQUIRED TO NEUTRALIZE RESIDUES.

	cc.	*cc.*	*cc.*	*cc.*		*cc.*
1	37.60	28.28	41.80	52.20		39.05
2	22.45	13.67	20.80	30.30		21.90
3	22.10	6.90	14.35	25.80		17.38
4	20.40	5.02	11.78	23.70		15.02

Again, the greatest loss of acetic acid is shown between the first and second evaporations, a smaller amount between the second and third, and a still smaller amount between the third and fourth, not exceeding, in the latter case, 0.02 gram per 100 cc in any case. In four out of the five cases it amounts to only 0.01 gram per 100 cc. In view of these facts, the associate referee recommends that in determining solids in vinegar three evaporations be carried out on the steam bath before drying in the oven. This number seems to be essential, but unnecessary evaporations are to be avoided because of loss in weight due to other causes than the volatilization of acetic acid. There seems to be no good reason why solids in vinegar should not be determined exactly as in wines (except for the repeated evaporations) using 50 cc of the sample when the solids are less than 3 grams and 25 cc when over 3 grams per 100 cc. In addition to the obvious advantage of having only one procedure for both wines and vinegars, the residues could be directly ignited for the ash, alkalinity, and phosphoric acid determinations, whereas by the present method of determining solids, using 10 cc of the sample, a separate and larger portion must be evaporated and ignited for the determination of phosphoric acid.

It was stated in last year's report that in determining reducing sugars in vinegar it might be found possible to omit clarification and make the determination directly on the filtered vinegar, without appreciably affecting the results. The results of the work on which this statement was based are given in Table 3.

TABLE 3.—*Effect of clarification and of neutralizing acetic acid on the determination of reducing sugars in vinegar.*

[Grams per 100 cc.]

Sample number.	Without clarifying and without neutralizing.	Without clarifying but after neutralizing.	After clarifying and removing lead, but without neutralizing.	Sample number.	Without clarifying and without neutralizing.	Without clarifying but after neutralizing.	After clarifying and removing lead, but without neutralizing.
1	1.43	1.42	1.42	7	0.69	0.70	0.70
2	1.34	1.33	1.32	8	.61	.62	.63
3	.92	.92	.94	9	.59	.61	.59
4	.82	.81	.84	10	.17	.18	.16
5	.80	.80	.79				
6	.73	.73	.70	Average	.810	.812	.809

Samples containing widely varying amounts of sugar were selected. The reducing sugars were determined by Munson and Walker's method and calculated as invert sugar. A comparison of the average results obtained shows that when the results are expressed to two places of decimals, as is usually done, it makes no difference whether the vinegar is clarified or not. It is also quite unnecessary to neutralize the acetic acid before making the determination.

During July, 1910, a sample of vinegar was sent to each of the United States food and drug inspection laboratories by the New York laboratory,[1] with the request that a complete analysis be made according to the procedure given in a letter which accompanied the sample. It was requested among other things that the reducing sugars be determined with and without clarification and the results carried out to three place decimals. The results which were reported on this particular sample showed that the amount of sugar found after clarification was slightly less than that found when the sample had not been clarified; but when carried out to two place decimals only, the difference was negligible. In reporting his results on this sample, E. R. Lyman, of the Portland laboratory, made the following statement: "We have found in this labora-

[1] The reports on this sample were furnished by the chief of the New York laboratory for use in making this report.

tory by repeated trials that the results on reducing sugars are identical, whether the sample is first clarified or not."

In last year's report mention was also made of the fact that it had been found that when a vinegar was subjected to steam distillation the distillate possessed the power to reduce Fehling's solution, probably due to some volatile substance having reducing properties, originally present in the vinegar. Unless this fact were taken into account, the values given for the reducing sugars, determined in the usual way, might be very seriously in error. Farnsteiner [1] seems to have been one of the first to report this.

For the purpose of getting additional data on this point, six different samples of vinegar were examined at the associate referee's laboratory. They were the same six samples procured in Nashville and previously mentioned in this report. The results obtained by Mr. Grab are given in Table 4.

TABLE 4.—*Effect of distillation on determination of reducing sugars (Grab.)*

Sample number.	A. Usual method.	After distillation.		Column A corrected.
		B. With steam.	C. Without steam.	
1.....	0.75	0.075	0.080	0.67
2.....	.61	.081	.083	.53
3.....	1.26	.171	.165	1.09
4.....	.88	.092	.103	.78
5.....	.89	.087	.097	.80
6.....	.74	.078	.085	.66

Column A of this table gives the reducing sugars determined in the original vinegar in the usual way. The results given in Column B were obtained by distilling 100 cc of vinegar with steam until 100 cc of distillate were collected. The reducing power of this distillate was then determined and expressed as grams invert sugar per 100 cc vinegar. Column C gives the results obtained by distilling 200 cc of vinegar without steam until 100 cc of distillate had been collected. The reducing power of the distillate was then determined and calculated as grams of invert sugar per 100 cc of original vinegar.

The two series of results in Columns B and C are practically identical when carried out to two decimal places. It is clear either that there is originally present in the vinegar a volatile substance having the power to reduce Fehling's solution or that some material is present which decomposes into volatile substances on distilling at atmospheric pressure. If the former is true, then the value, 1.26, obtained by the usual method for sample No. 3 would have to be corrected by deducting 0.17 gram, an amount which certainly can not be neglected. A distillation in vacuo at as low a temperature as possible, it is believed, would show whether or not the volatile substance is present as such in the vinegar. The referee did not have time to determine this point. If it is found that the volatile substance is present as such in the vinegar, either a correction must be applied, and the amount of this correction determined in each case by a distillation and determination of the reducing power of the distillate, or some means of getting rid of this volatile substance before determining the reducing sugars will have to be found. Two evaporations, as in the method given for the removal of alcohol in vanilla extracts, previous to the determinations of vanillin, etc. (Bulletin 107, Revised, p. 156), are not sufficient to do this. It is possible that evaporation on the steam bath to a sirupy consistency as in the determination of solids might suffice. The residue could then be dissolved in water, made up to the original volume, and the reducing sugars determined in this solution.

[1] Zts. Nahr. Genussm., 1899, 2: 198-209.

In the procedure which accompanied the letter sent out with the sample from the New York laboratory, previously mentioned, two determinations were included which have recently been applied to the analysis of vinegar, namely, the amount of alcohol precipitate and the pentosans. The 15 results reported for pentosans are most encouraging, as all lie within the values 0.11 and 0.13 gram per 100 cc, showing that this determination is susceptible of a very considerable degree of accuracy. When sufficient data for the fixing of approximate limits become available, this determination may be of great service in indicating the material from which the vinegar is made. The same may be said of the alcohol precipitate determination, although the 18 results reported do not agree among themselves so well, varying between 0.08 and 0.27 gram per 100 cc. Some of the analysts, however, had had no experience with either of these determinations, and with more practice the results on a given sample should agree more closely.

Twelve results for glycerin were reported on this sample, and considering the length and tediousness of the method, they are very satisfactory. A paper on the Determination of Glycerin in Vinegar and Characteristic Glycerin Ratios, by S. H. Ross, of Omaha, is published in these Proceedings (see following paper). The determination may prove to be of value.

The results on the removal of color by fuller's earth were far from satisfactory, the figures reported varying in the amount of color removed from practically none to 64 per cent. As each laboratory used the fuller's earth which it happened to have, it is quite probable that the extreme variations in the results reported are due to the different qualities of earth. It was found that in using 10 grams of earth and 50 cc of vinegar, about as much color was removed as when 25 grams of earth were used, and the smaller amount has the decided advantage of giving a greater quantity of filtrate, which is more easily and accurately matched with diluted solutions of the original vinegar, owing to the fact that it contains less color formed by reaction between the fuller's earth and the vinegar. It is suggested that in the future when collaborators are asked to make this determination, they be furnished with fuller's earth taken from a large stock of a sample found to be suitable for the purpose. It is believed that this is the only way in which comparative results of any value can be obtained.

DETERMINATION OF GLYCERIN IN VINEGAR AND CHARACTERISTIC GLYCERIN RATIOS.

By S. H. Ross.

The modified method [1] for the determination of glycerin in wine was applied to the determination of glycerin in vinegar. Since several changes were made, the method adopted is submitted in detail.

Method for the Determination of Gylcerin in Vinegar.

EXTRACTION.

Make all evaporations on a water bath, the temperature of which is maintained between 85° and 90° C. Evaporate 100 cc of vinegar to about 5 cc, add 20 cc of water and again evaporate to about 5 cc, in order to expel acetic acid. Treat the residue with about 5 grams of fine sand and with 15 cc of milk of lime (freshly prepared and containing about 15 per cent of calcium oxid), and evaporate almost to dryness with frequent stirring (avoid formation of dry crust or evaporation to complete dryness). Treat the moist residue with 5 cc of hot water, rub into homogeneous paste, and then add 45 cc of absolute alcohol, washing down the sides of the dish to remove adhering paste, and stir thoroughly. Heat the mixture on a water bath, with constant stirring, to incipient boiling, and decant the liquid through a 12.5 cm fluted filter into a porcelain dish. Wash the residue repeatedly with small portions of hot 90 per cent alcohol, twice by decantation, then transfer all of the material to the filter and con-

[1] U. S. Dept. Agr., Bureau of Chemistry Bul. 132, p. 85.

tinue washing until the filtrate amounts to about 150 cc. To save time the first 75 cc of the filtrate may be placed on a water bath to evaporate while the second 75 cc is being collected, the last is then added to the first portion. Evaporate to a sirupy consistency, add 10 cc of absolute alcohol to dissolve the residue, and transfer to a 50 cc glass-stoppered cylinder, using two additional portions of 5 cc each of absolute alcohol to wash out the dish and complete the transfer. Add three portions of 10 cc each of absolute ether, thoroughly shaking after each addition. Let stand until clear, then pour off through a filter, and wash the cylinder and filter with a mixture of one part of absolute alcohol to one and one-half parts of absolute ether, pouring the wash liquor also through the filter. If a heavy precipitate is observed in the cylinder it is advisable to centrifuge at low speed and decant the clear liquid through a filter. Add 20 cc of the mixture of absolute alcohol and absolute ether (1:1.5) to the precipitate in the cylinder, shake thoroughly, centrifuge and decant; repeat this process three times. Evaporate the filtrate and washings to about 5 cc on the water bath, add 20 cc of water and evaporate to about 5 cc; again add 20 cc of water and evaporate to about 5 cc; finally add 10 cc of water and evaporate to about 5 cc. (These evaporations are necessary to remove all the ether and alcohol and when conducted at 85° to 90° C. there is no loss of glycerin up to 50 per cent concentration.) Transfer the residue with hot water to a 50 cc volumetric flask, cool, add silver carbonate freshly precipitated from 0.1 gram of silver sulphate, shake occasionally, and allow to stand 10 minutes; then add 0.5 cc of lead subacetate solution, shake occasionally, and allow to stand 10 minutes; make up to the mark, shake well, filter, rejecting the first portion of the filtrate, and pipette off 25 cc of the clear filtrate into a 250 cc glass-stoppered volumetric flask. Add 1 cc of concentrated sulphuric acid to precipitate the excess of lead (which otherwise would subsequently combine with part of the standard bichromate and cause an error). Then determine the glycerin by the following method:

DETERMINATION OF GLYCERIN BY A MODIFICATION OF HEHNER'S BICHROMATE OXIDATION METHOD.[1]

(a) *Solutions required.*—(1) Strong bichromate: Dissolve 74.56 grams dry, recrystallized potassium bichromate in water, add 150 cc concentrated sulphuric acid, cool, make up to 1,000 cc at 20° C., and determine the specific gravity of the solution at 20°/20° C.; 1 cc of this solution equals 0.01 gram glycerin. The high coefficient of expansion of this strong solution makes accurate volumetric measurement difficult on account of the changes in room temperature from day to day and it is therefore advisable to take the specific gravity and use weighed amounts of the solution, which may be conveniently introduced into the tests by means of a weight burette. Then the weight of the solution used in a given test, divided by the specific gravity, equals the volume used. The strong bichromate solution has an apparent expansion in glass of 0.0005 (or 0.05 per cent) for each degree centigrade. By observing this correction the solution may be measured in the absence of a weight burette.

(2) Dilute bichromate: Introduce a weighed amount (12.5 times the specific gravity) of the strong bichromate from a weight burette into a 250 cc glass-stoppered volumetric flask, dilute with water, and make up to the mark at room temperature; 20 cc of this solution is equivalent to 1 cc of the strong bichromate. If the weight taken is slightly in excess of the 12.5 cc equivalent, make up to the mark and then add required amount of water to make one-twentieth dilution.

(3) Ferrous ammonium sulphate: Dissolve 30 grams of crystallized ferrous ammonium sulphate in water, add 50 cc of concentrated sulphuric acid, cool, and dilute to 1,000 cc at room temperature; 1 cc of this solution is approximately equivalent to 1 cc of the dilute bichromate. Its value changes slightly from day to day and should be standardized against the dilute bichromate whenever used.

(b) *Oxidation of glycerin.*—From a weight burette introduce into the 250 cc flask, containing the 25 cc purified glycerin solution, a weighed amount of the strong bichromate solution, sufficient to leave about 12.5 cc excess (with ordinary vinegars purified as above use 30 to 35 cc), carefully add 24 cc of concentrated sulphuric acid, rotating flask gently to mix contents and avoid violent ebullition, then place in boiling-water bath for exactly 20 minutes. Remove flask from bath, dilute at once, cool, and make up to mark at room temperature. A slightly more accurate oxidation may be obtained by adding only 15 cc of concentrated sulphuric acid and continuing the digestion for at least 2 hours in a boiling-water bath.

(c) *Titration.*—(1) Standardize the ferrous ammonium sulphate solution against the dilute bichromate solution by introducing from the respective burettes approximately 20 cc of each of the two solutions into a beaker containing 100 cc of distilled

[1] Richardson and Jaffé, J. Soc. Chem. Ind., 1898, 17: 330, modified by W. H. Low.

water. Complete the titration, using potassium ferricyanid solution as the indicator on a porcelain spot plate. From this titration calculate the volume (F) of ferrous ammonium sulphate equivalent to 20 cc of the dilute solution and also, therefore, to 1 cc of the strong bichromate solution.

(2) In place of the dilute bichromate solution now substitute a burette containing the oxidized glycerin with excess bichromate solution, and ascertain how many cubic centimeters of it are equivalent to (F) cubic centimeters of the ferrous ammonium sulphate solution, and also, therefore, to 1 cc of the strong bichromate. Then 250 divided by this last equivalent equals the number of cubic centimeters excess of the strong bichromate solution present in the 250 cc flask after oxidation of the glycerin.

(3) The number of cubic centimeters of strong bichromate added, minus the excess found after oxidation, multiplied by 0.01 gram, equals the weight of glycerin in the 25 cc of purified solution used in the determination; this result, multiplied by 2, gives the weight of glycerin in grams per 100 cc of the vinegar.

Duplicate determinations of glycerin were made by this method on the following samples of known purity:

A. Sample of cider stock.

B. Sample of mixture from generator (2 parts A, 3 parts C).

C. Sample of finished cider vinegar made from A.

Glycerin determinations on cider stock and vinegar.

[Grams per 100 cc.]

Sample.	Glycerin.	
	Duplicates.	Average.
A.....	{0.355 .368}	0.362
B.....	{ .329 .334}	.332
C.....	{ .311 .306}	.309

The amounts of glycerin found in A, B, and C indicate that during the process of oxidation of alcohol to acetic acid, in the generator, there is also an appreciable oxidation of the glycerin. A more complete analysis of each of the samples was then made for the purpose of calculating ratios based on the glycerin content.

Glycerin formed in alcoholic fermentation is usually expressed as glycerin-alcohol ratio, or vice versa. However, since cider stock and vinegar samples contain varying amounts of alcohol and acetic acid formed therefrom, the following formula was considered preferable for calculating and expressing the ratio based upon these constituents:

$$R=\frac{(A\div 0.046)+(V\div 0.06)}{(G\div 0.0307)},$$

in which R=ratio of combined alcohol-and-acid to glycerin on equivalent basis; A=alcohol (normal equivalent, 0.046); V=volatile acid (acetic) (normal equivalent, 0.060), and G=glycerin (normal equivalent, 0.0307), all expressed in grams per 100 cc of sample.

The ratio of total solids to glycerin was also considered characteristic.

Analysis of cider stock and vinegar showing glycerin ratios.[1]

Sample.	A.	B.	C.	Sample.	A.	B.	C.
Alcohol (per cent by volume)	5.69	1.96	0.25	Reducing sugar as invert	0.38	0.44	0.53
Alcohol	4.52	1.56	.20	Per cent sugar in solids	14.3	19.5	24.9
Glycerin	.36	.33	.31	Ash	.34	.35	.35
Volatile acid	.46	3.63	5.13	Ratio combined alcohol-and-acid to glycerin on equivalent basis	9.1	8.7	8.9
Fixed acid	.14	.07	.02	Ratio solids to glycerin	7.4	6.8	6.9
Solids	2.65	2.26	2.13				
Nonsugar solids	2.27	1.82	1.60				

[1] All measurements made at 20° C. and results reported in grams per 100 cc, except when otherwise noted.

A sample of alleged cider vinegar, which, however, was undoubtedly spurious, was found to contain 0.07 gram of glycerin and 1.87 grams of solids per 100 cc. The ratio of solids to glycerin on this sample was therefore nearly 27, which is a striking increase above the corresponding ratio found on samples of known purity.

While not enough analyses have been made to establish definite limits, it is believed that the determination of glycerin and the use of the two ratios suggested will furnish additional means of judging the purity of vinegar.

REPORT ON FLAVORING EXTRACTS.

By E. M. Chace, *Associate Referee.*

Plan of Work.

At the meeting in 1909 the referee on flavoring extracts placed before this association a set of methods for the examination of lemon and orange oils, giving notice that he would ask for their provisional adoption at the next meeting of the association. These methods were printed in the report for that year (Bulletin 132, p. 97).

For the determination of citral, the fuchsin sulphite method, as given for flavoring extracts, was recommended, as it was considered the best method available at the time. When this method was first devised, however, attention was called to the fact that on lemon oils the multiplication of the error was so great as to impair to a considerable degree its accuracy. At that time a method had recently been devised by A. H. Bennett, of Catania, Sicily, for the determination of aldehydes in lemon oil, using hydroxylamin, and, somewhat later, an unpublished method devised by Dr. Kleber, using phenyl hydrazin as a reagent, was called to the attention of the referee. Dr. Kleber very kindly gave his consent to the use of the method although he had not published it, preferring to wait until he had done further work on other aldehydes.

It is highly desirable to have an accurate method for this determination in general use in order that it may be included if possible in the revision of the Pharmacopœia as well as adopted by this association. The work for the year was therefore confined to testing four methods for citral determination. Both the fuchsin sulphite and Hiltner's metaphenylene diamin methods have been satisfactory in the determination of the aldehydes and citral in citrus fruit extracts, but, for the reason just stated, they were not considered so satisfactory for work on essential oils.

A description of the methods was sent to 15 chemists, who had offered to collaborate, with the following samples:

Sample No. 1 was an old lemon oil made up of composite samples collected in Sicily in 1907. There appeared to be some indication in former work, both at the Washington and at the Denver laboratories of the Bureau of Chemistry, that old oils would give high results by the fuchsin sulphite method and low results by the Hiltner method, owing to the breaking down of compounds, with the formation of aldehyde determined by the fuchsin sulphite procedure but not determined by the Hiltner method.

Sample No. 2 was a commercial oil which had been tested and found to comply with the standards.

Sample No. 3 had as a base the same oil that was used in Sample No. 2, but to 1,200 grams of the sample were added 12 grams of citral, making approximately 1 per cent more aldehyde in Sample No. 3 than in Sample No. 2.

Sample No. 4 was a factitious product containing 94 per cent of specially purified limonene free from citral, 4.27 per cent of citral, 0.50 per cent of citronellal, 0.50 per cent of geraniol, 0.50 per cent of geranyl acetate, and 0.25 per cent of linalool acetate, the whole colored with a trace of turmeric.

The following methods were sent to the collaborators for study: Hiltner's metaphenylene diamin method (p. 70), Kleber's phenyl hydrazin method (p. 72), Chace's fuchsin sulphite method (Bulletin 122, p. 32, or Circular 43, p. 10), dissolving an equivalent amount of lemon oil in aldehyde-free alcohol, and Bennett's hydroxylamin method (Analyst, 1909, 34: 14), which reads as follows:

Reagents: Half-normal hydrochloric acid.

Normal alcoholic potash.

Half-normal hydroxylamin in 80 per cent alcohol. This solution should be standardized against the half-normal hydrochloric acid.

Manipulation: Mix 15 grams of the sample with 20 cc of the hydroxylamin solution and add 8 cc of alcoholic potash solution and 20 cc of 95 per cent alcohol. Boil under a reflux cooler for half an hour and cool. Wash down the condenser and dilute the sample to approximately 250 cc with water and neutralize to phenolphthalein. Titrate with half-normal hydrochloric acid, using methyl orange, and test the end point by the use of drops of a very dilute indicator upon a white plate. Run a blank determination and calculate the amount of citral from the number of cubic centimeters of acid used in this blank minus that used in the determination, multiplying the difference by 0.076. The result is the weight of the citral present.

Analytical Results.

The results received from seven analysts, five outside of the Washington laboratory, are given in the following table:

Cooperative results on citral.

Analyst No.	Sample No. 1.				Sample No. 2.			
	Hiltner method.	Chace method.	Kleber method.	Bennett method.	Hiltner method.	Chace method.	Kleber method.	Bennett method.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
1	3.49							
	3.33				4.47			
	3.05	4.00			4.05	4.38		
	3.00	4.38			4.15	5.00		3.95
	3.33	4.69	4.00	3.60	3.75	4.69	4.46	4.15
2	4.19	5.15	4.40	4.51	4.27	5.44	4.60	4.52
	4.21	5.58	4.47	4.47	4.19	5.37	4.60	4.57
3	4.01	6.01	4.45				4.56	
			4.63	4.48	4.62	6.02	4.90	4.33
4	4.53	4.60	4.56	4.46	4.45	4.68	4.61	4.31
5	4.50	4.74	4.05	4.75	4.54	4.62	4.37	4.68
	4.59	4.85	4.65	4.74	4.61	4.65	4.62	4.61
6	3.83	3.95	4.25	4.00				
			4.25	4.05				
7	3.39	5.39	4.37	6.29	3.52	5.56	4.61	6.36
Maximum	4.59	6.01	4.65	6.29	4.62	6.02	4.90	6.36
Minimum	3.00	3.95	4.00	3.60	3.52	4.38	4.37	3.95
Difference	1.59	2.06	.65	2.69	1.10	1.77	.53	2.41
Average of analysts' averages	3.80	4.85	4.37	4.53	4.24	5.04	4.59	4.61
Average of individual results	3.95	4.92	4.36	4.59	4.25	5.17	4.59	4.71

Cooperative results on citral—Continued.

Analyst No.	Sample No. 3.				Sample No. 4.			
	Hiltner method.	Chace method.	Kleber method.	Bennett method.	Hiltner method.	Chace method.	Kleber method.	Bennett method.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
1	5.00							
	5.00	5.00			4.42	4.50		
	5.30	5.60		4.76	3.65	5.00		4.91
	5.00	5.00	5.12	4.56	4.54	4.69	4.15	4.25
2	5.06	6.10	5.28	5.22	4.79	5.93	4.51	4.62
	5.33	6.12	5.28	5.31	4.66	6.02	4.39	4.68
3			5.31				4.26	
	5.84	6.84	5.90	5.54	6.22	6.30	3.86	5.60
4	5.04	5.26	5.22	4.86		4.76	4.46	4.85
5	5.72	5.83	4.90	5.77	{ 6.36 / 6.20 }	6.23	4.06	6.02
	5.84	5.93	5.82	5.69	6.34	6.21	4.50	5.62
6	4.72	4.72	5.32	5.07				
			5.37	5.07				
7	4.98	5.86	5.47	5.77	4.06	5.37	4.17	6.16
Maximum	5.84	6.84	5.90	5.77	6.34	6.30	4.51	6.16
Minimum	5.00	4.72	4.90	4.56	3.65	4.50	3.86	4.25
Difference	.84	2.12	1.00	1.21	2.69	1.80	.65	1.91
Average of analysts' averages	5.24	5.66	5.36	5.24	5.12	5.50	4.26	5.19
Average of individual results	5.23	5.69	5.34	5.27	5.10	5.56	4.26	5.28

It will be seen at a glance that the two colorimetric methods are more troublesome than the methods using titration, the Hiltner method giving uniformly low results and the fuchsin sulphite method uniformly high results as compared with the other two. The differences between the highest and the lowest result obtained is also uniformly higher by these two methods than by the others. It was thought that trouble would be encountered in determining the end point in the Bennett method, and it is quite evident that some of the analysts found this difficulty practically insurmountable. If the directions are followed, however, with the Kleber method, the difficulty encountered does not seem to have been nearly so great. Many of the averages would be considerably modified by the elimination of the results of a single analyst; as, for instance, the results of analyst No. 7 are uniformly much too high using the Bennett method, as are the results reported by analyst No. 4 on the fuchsin sulphite method.

COMMENTS OF ANALYSTS.

E. R. Lyman, Portland, Oreg.: The results obtained by the colorimetric methods of Hiltner and Chace are not satisfactory; duplicate determinations made at different times and with freshly made reagents and oil solution showing very considerable variations, but since repeated duplication does not seem to better matters, the results as obtained are sent. In the Chace method, I am not sure but that the rise in temperature when the alcohol is diluted with the fuchsin reagent is the cause of the trouble. Although the bath is kept at 15° C. the temperature rises to nearly 20° C. when the solutions are mixed. I find it next to impossible to distinguish with certainty standards differing as little as 0.25 mg. This range of uncertainty may make a difference of over 0.5 per cent on the ordinary 4 per cent oil and seems inherent in the method. Kleber's method was found to give a good end point when an excess of acid was added and titrated back after washing the acid from the oil as directed. In the Bennett method the end point was definite to 0.1 cc without testing on a white plate as directed.

It is not thought that the difficulty encountered by Mr. Lyman is due to the rise of temperature, as experimental work last year by Mr. Mory showed that the temperature was not a factor.

C. F. Jablon, New York, N. Y.: The only difficulty encountered was with the Bennett determination, as the end point with phenolphthalein could not be observed closely. To overcome this, the analyst followed a method suggested by Seeker; neutralizing the alcoholic solution of the oil with alcoholic potash using phenolphthalein before adding the hydroxylamin and alcoholic potash, the digestion being conducted as directed, the necessity of neutralizing the phenolphthalein was obviated, giving a perfectly white emulsion which could be easily titrated directly.

R. S. Hiltner, Denver, Colo., states that all of the samples worked normally with the exception of No. 1, in which, when using his method an abnormal yellowish green color was produced on adding the reagent. He attributes this to the use of commercial limonene as one of the ingredients of the sample, but it is more likely to have been due to by-products caused by deterioration of the sample owing to age, as no commercial limonene was used, the sample being genuine in every respect. He believes the result given on this sample to be much too high; it is, however, quite close to the average where the second set of averages are taken. The principal objection found by this analyst to the Kleber method is that it is difficult to determine the exact end point in the titration. He also notes that the acid value of the four samples differed widely and that perhaps the neutralization of this acidity would be advisable where the Kleber and Bennett methods are used. All of the work was done early in May except that on the Bennett method, which was not tried until August.

Mr. Hiltner reported the following results by the paraphenylene diamin method: Sample No. 1, 4.32 per cent; sample No. 2, 4.99 per cent; sample No. 3, 6.06 per cent; sample No. 4, 4.73 per cent.

F. D. Merrill, San Francisco, Cal., could not determine the citral in sample No. 4 by Hiltner's method owing to the formation of a green color in the tube containing the solution of the sample. This difficulty was encountered by one other collaborator.

H. J. Wichman, Galveston, Tex., found difficulty in obtaining trustworthy results on samples Nos. 1 and 4 by the Hiltner method, the color developed being of a different tint than that of the standard. This difference largely increased on standing. A similar difficulty was noticed by the fuchsin sulphite method on the same samples, the color deepening much more rapidly in the sample than in the standard. With the Kleber method he had some difficulty with the preparation of the reagent, as both the phenyl hydrazin sent out from Washington and that on hand in Galveston gave considerable color when mixed with absolute alcohol, rendering the end point somewhat obscure. He found no difficulty in detecting the end point with the hydroxylamin method, using a dilute solution of methyl orange on a white plate.

A. R. Albright found considerable difficulty in obtaining a definite end point by the Bennett method.

C. P. Wilson, Washington, D. C., did not encounter this trouble.

Considering the results as a whole, the Kleber method seems to give not only more closely agreeing figures, but also less difficulty in the hands of the analyst generally, and it is believed that the method should be provisionally adopted. The average results by this method and by the Bennett method are very close and it is quite possible that with some further study the Bennett method will prove an acceptable optional method to many analysts. The colorimetric methods do not seem to compare favorably with others; one giving somewhat low results and the other results which are considerably too high. While the latter error is always in favor of the sample examined, a method giving more accurate results is certainly desirable.

Recommendations.

In addition to the methods for examination of lemon and orange oils, the associate referee has the following recommendations to make. Copies of these recommendations have been sent to many of the prominent food analysts throughout the United States and the comments which they have made are included in the report.

(1) It is recommended that the following text be substituted for all matter under the heading "4. Determination of vanillin, coumarin, and acetanilid."[2]

4. Determination and Identification of Vanillin and Coumarin.

hess and prescott method for vanillin and coumarin.

Weigh 50 grams of the extract directly into a tared 250 cc beaker with marks showing volumes of 80 and 50 cc, dilute to 80 cc. and evaporate to 50 cc in a water bath kept at 70° C. Dilute again to 80 cc with water and evaporate to 50 cc. Transfer to a 100 cc flask, rinsing the beaker with hot water, add 25 cc of standard lead acetate solution (80 grams of normal lead acetate made up to one liter), make up to the mark with water, shake, and allow to stand overnight. Decant on a small dry filter, pipette off 50 cc of filtrate, and extract, shaking four times in a separatory funnel using 15 cc of ether each time. Wash the combined ether solutions four or five times with 2 per cent ammonium hydroxid, using 10 cc the first time and 5 cc thereafter. Slightly acidulate the combined ammoniacal solutions with hydrochloric acid, cool and extract in a separatory funnel with four portions of ether, using about 40 cc altogether. Evaporate the ethereal solutions at room temperature, dry over sulphuric acid and weigh. If the residue is discolored or gummy, reextract in the dry state with boiling petroleum ether (b. p. 40° C. or below) not less than fifteen times, evaporate the solvent, dry and weigh. The residue should now be white, crystalline vanillin with a melting point of approximately 80° C. A small amount of this residue dissolved in 2 drops of concentrated hydrochloric acid upon the addition of a crystal of resorcin should develop a pink color.

Evaporate the original ether extract of the sample after removal of the vanillin with ammonium hydroxid at room temperature and dry over sulphuric acid. The residue, if pure coumarin, should melt at approximately 67° C., and should respond to Leach's test for coumarin as follows: A small portion of the residue dissolved in hot water and filtered should develop a brown precipitate upon the addition of a few drops of tenth-normal iodin in potassium iodid. This precipitate finally gathers in green flecks, leaving a clear brown solution. The reaction is especially marked if the reagent is applied with a glass rod to a few drops of the solution on a white plate or tile.

It will be seen that the method is practically that of Hess and Prescott as modified by Winton and Bailey, with the exception that the troublesome variations made necessary by the examination for acetanilid are omitted. It is not deemed necessary to include this determination, inasmuch as at the present time no such adulteration is taking place. The method also omits, of course, the tests for acetanilid. Commenting on the proposed change, R. E. Remington, of the North Dakota Agricultural College, says:

In using the Hess and Prescott method for vanillin and coumarin I have found the residue often slightly yellowish in color, but seldom oily. It is found invariably contaminated by ammonium chlorid, due to the slight solubility of this salt in ether which contains water. I have found it necessary to take up the residue with anhydrous ether and again evaporate in a tared dish, the extraction with hot petroleum ether serving the same purpose. I have never been able to obtain a satisfactory reaction with Leach's test for coumarin either with C. P. coumarin or with that obtained from vanilla extracts containing it.

In the laboratories of the Bureau of Chemistry it has been generally found that wherever anhydrous ether could be used in purifying the vanillin it was a better solvent than hot petroleum ether. In some grades of extracts, however, especially those containing sugar, the petroleum ether gives a much purer product, and is satisfactory if used repeatedly. It does not seem that the fault found by Mr. Remington with Leach's test for coumarin is common.

Mr. Hiltner, of the Denver laboratory, suggests that 25 cc of the sample be measured instead of 25 grams weighed as proposed, since the results for extracts are now commonly stated in grams per 100 cc. He has noted that the lead precipitate formed in vanillas is not appreciably soluble in ether, and hence it is not necessary to filter and wash as directed, this being a very tedious operation which can be omitted without sacrificing accuracy. If the lead acetate be added slowly and the solution vigorously stirred the precipitate is formed in a finely-divided state and will run through the aperture of a separatory funnel without clogging. Another point is made that the commercial vanilla extracts now on the market seldom, if ever, contain coumarin unless declared upon the label, hence it seems unnecessary to carry on that portion

of the method which has the separation of vanillin and coumarin for its object. The purity of the dried ether extract could be readily determined by its physical properties and the absence of coumarin proved by Leach's method.

Mr. Schulz, of the Detroit food and drug inspection laboratory, also suggests that it would be better to measure than to weigh the portions of the extract used for analysis.

Mr. Brinton suggests the use of pentane in place of gasoline. It boils very close to 40° C., and obviates the necessity of distilling large quantities of gasoline in order to obtain a small amount of low boiling point material.

Mr. Lyman, of the Portland food and drug inspection laboratory, makes the following comments:

It has been my experience that the filtration of the extract solution after the addition of lead acetate is slow, permitting the solution to cool down unless a hot filter is used. I have found filtering under pressure, using a platinum cone, to be very satisfactory. When the precipitate is on the filter I fill the filter with hot water and break up the precipitate with the loop of a moderately stiff platinum wire. By repeating this two or three times I feel sure that the precipitate is free from vanillin or coumarin. I have a large test tube of the right length and marked for 50 centimeters, which I put inside the filter flask to receive the filtrate.

(2) It is recommended that the following be added under "11. Test for coloring matter (caramel)," page 159, of Bulletin 107, Revised.

(*c*) Woodman and Newhall's Method.

Mix 15 cc of the extract with 2 cc of a 5 per cent solution of zinc chlorid, add 2 cc of 2 per cent potassium hydroxid solution and filter. Wash the precipitate with hot water, dissolve in 15 cc of 10 per cent hot acetic acid, neutralize, concentrate the filtrate to one-half its original volume, and divide into two parts. To 1 part add 3 parts of paraldehyde and enough alcohol to render homogeneous; to the other part add an equal part of a mixture of 2 parts phenyl hydrazin hydrochlorid, 3 parts sodium acetate, and 20 parts of water. After standing overnight both solutions will develop a brown flocculent precipitate if caramel be present.

Mr. Hilts, of the Philadelphia laboratory, suggests washing with water or decanting twice and settling with the aid of a centrifuge in this method. A little common salt may be added to the wash water if the precipitate does not readily settle, but in this case the acetic acid solution should be filtered either before or after concentration. He has often used this manipulation because the filtration when washing on paper is sometimes very tedious. Mr. Hilts also questions whether the precipitate formed overnight in the paraldehyde test is not accurately described as flocculent, preferring the term "adherent brown precipitate;" and is further of the opinion that the paraldehyde test is better for caramel, having had little success with the phenyl hydrazin hydrochlorid modification.

Mr. Loomis, of the Seattle food and drug inspection laboratory, suggests the following slight modification for the Woodman-Newhall method:

Mix 15 cc of the extract with 2 cc of a 5 per cent solution of zinc chlorid; add 2 cc of a 2 per cent solution of potassium hydroxid, and filter. Wash the precipitate with hot water, dissolve on the filter in 15 cc or less of hot acetic acid, nearly neutralize, concentrate the solution to one-half its original volume, filter if necessary, and divide into 2 parts. To 1 part add 3 parts of paraldehyde and enough alcohol to render the liquid homogeneous, etc.

(3) It is recommended that the heading "Lemon extract" be changed to "Lemon and orange extracts," and that the heading "4. Lemon oil" be changed to "Lemon and orange oil" (Bulletin 107, Revised, pp. 159 and 160).

(4) It is recommended that the following text be substituted for "(*a*) By polarization (Mitchell)," on page 160, Bulletin 107, Revised.

Polarize the extract at 20° C. without dilution in a 200 mm tube. Divide the reading in degrees Venske by 3.2 in the case of lemon extract and by 5.2 in the case of orange extract; in the absence of other optically active substances the result will be the percentage of oil by volume. A small amount of cane sugar is occasionally present; if so, determine it as directed under "Sucrose" and correct the reading accordingly.

(5) It is recommended that the last two paragraphs under "(*b*) By precipitation" be omitted (loc. cit.).

Regarding the precipitation method, Mr. Remington says:

I have always been opposed to the arbitrary adding of 0.4 or any number to the amount of lemon or orange oil obtained by precipitation. The factors which control the amount of oil left in solution and in suspension are temperature, concentration, and rate and time of centrifuging. I always insist that the correction factor be worked out for the particular speed, temperature, and concentration which we use. * * * I feel sure that variations in the amount of alcohol would play some part here also.

(6) It is recommended that "Refraction of precipitated oil," page 160, Bulletin 107, Revised, be omitted.

(7) It is recommended that the heading, "Determination of citral in lemon extract," be changed to "Determination of total aldehydes in lemon and orange extracts."

The text of these changes is practically that of the original, except for the fact that provision is made for the determination of orange oil in orange extract. The omission of "5. Refraction of precipitated oil" is made for the reason that experience has shown that this figure is likely to lead to erroneous conclusions. It will differ very materially with the percentage of alcohol contained in the flask and apparently with other conditions not yet fully understood. As a rule the figures are at least two points lower in the third decimal place than the correct figures for lemon or orange oil.

(8) It is recommended that the following method be provisionally adopted:

DETERMINATION OF CITRAL IN LEMON AND IN ORANGE EXTRACTS (HILTNER).

Reagents.—Metaphenylene diamin hydrochlorid solution: Prepare a 1 per cent solution of metaphenylene diamin hydrochlorid in 95 per cent alcohol. Decolorize if necessary by shaking with fuller's earth; filter through a double filter. The solution should be bright and clear, free from suspended matter, and practically colorless. It is well to prepare only enough solution for the day's work as it darkens on standing.

Alcohol.—For the analysis of lemon extracts, 90 to 95 per cent alcohol should be used, but for terpeneless extracts, alcohol of 40 to 50 per cent strength is sufficient. Filter to remove any suspended matter. The alcohol need not be purified from aldehyde. If not practically colorless, render slightly alkaline with sodium hydroxid and distil.

Apparatus.—Any convenient form of colorimeter may be used.

Manipulation.—All of the operations may be carried on at room temperature. Weigh into a 50 cc graduated flask, 25 grams of the extract and make up to the mark with alcohol (90 to 95 per cent). Stopper the flask and mix the contents thoroughly. Pipette into the colorimeter tube 2 cc of this solution, add 10 cc of metaphenylene diamin hydrochlorid reagent, and complete the volume to 50 cc (or other standard volume) with alcohol. Compare at once the color with that of the standard which should be prepared at the same time, using 2 cc of standard citral solution and 10 cc of the phenylene diamin reagent, and making up to standard volume with alcohol. From the result of this first determination calculate the amount of standard citral solution that should be used in order to give approximately the same citral strength of the sample under examination, then repeat the determination.

This method is now too well known to need comment, but attention is called to the fact that where determinations are constantly being made by both this method and the fuchsin-sulphite method some indication should be given as to which method is used in reporting results. If the heading used for the method is strictly followed in reporting, only citral as determined by this method will be reported as such, while, as determined by the fuchsin-sulphite method, it should be reported as total aldehydes. Upon orange extracts both methods should be used, inasmuch as the results on orange oils by the Hiltner method show a maximum content of 0.7 per cent, while by the fuchsin-sulphite method the aldehydes run as high as 2.5 to 3 per cent.

Attention was called last year to the fact that where sugar was used in the preparation of extracts the Hiltner method apparently gave low results. This should be borne in mind when testing such extracts, and comparative figures should be obtained using the fuchsin-sulphite method.

Mr. Hiltner, has also devised a similar method, using paraphenylene diamin as a reagent, and he has submitted the results already referred to in the report. The referee's experience indicates that the para reagent is not so delicate as the meta and is more likely to give varying colors between the standard and the sample.

(9) It is recommended that the following method be provisionally adopted:

10. Detection of Coloring Matter.

(a) lemon and orange peel color (albrech).

Place a few cubic centimeters of the extract in a test tube and add slowly three or four volumes of concentrated hydrochloric acid. Place a few cubic centimeters of the extract in a second tube and add several drops of concentrated ammonia. In the presence of lemon or orange peel color the yellow tint of the original extract will be materially deepened in both cases.

(b) turmeric.

Evaporate 25 to 50 cc of the extract upon a small piece of filter paper, dry at low temperature, and moisten with a weak solution of boric acid containing a small amount of hydrochloric acid. Upon drying a second time a cherry-red color, changing to green when spotted with ammonia, develops in the presence of turmeric.

Method (a) has not yet been published by Mr. Albrech and is read at this meeting for the first time. It has been tested in the laboratory in Washington, however, and his opinion that the general results are satisfactory confirmed. Mr. Remington, in commenting upon the method, says:

Regarding the proposed color reactions for lemon and orange extracts, I have found that hydrochloric acid, instead of deepening the color, lightens it materially. I have found the best test for these coloring matters to be ferric chlorid, which produces an olive-green coloration and, in some cases, after boiling, a reddish-brown precipitate. I have also found that bromin water decolorizes these extracts.

In discussing the proposed method, Mr. Albrech suggests this addition: "Dilute a few cubic centimeters of the extract until the yellow color practically disappears, place part in one test tube and part in a second test tube, add hydrochloric acid and ammonium hydroxid as described, and a resulting yellow tint in each case will result."

It would seem that in using the method for the first time the results thus obtained would probably be more striking than those by the suggested method. Albrech has found that the method worked well where an extract had been colored both with lemon peel and with Naphthol yellow S. The yellow color due to the anilin dye was bleached by the hydrochloric acid, and upon further addition of the reagent the yellow color due to the lemon peel was brought out.

The following method for the detection of natural color in orange and lemon extracts has been received by the associate referee from H. L. Schulz, of the Detroit laboratory:

Place 10 cc of the extract in a test tube and make strongly alkaline with sodium hydroxid. Shake and then add 10 cc of petroleum ether; shake thoroughly and allow to separate. The coloring matter will be precipitated or adhere to the sides of the tube. Pour off the solution, allowing it to remain behind, and wash with 95 per cent alcohol. Dissolve the residue in 5 cc of water. The color of this solution partly disappears upon the addition of a drop of hydrochloric acid, but upon further addition of hydrochloric acid increases until a clear amber color is produced. As the color is readily soluble in water, this test can not be applied to a terpeneless extract without first reducing the volume of water by evaporation and taking up with strong alcohol.

The test for turmeric should be included here inasmuch as the test given under "Coloring matter" is not sufficiently full for use on extracts. Some difficulty has been experienced in the detection of the trace of turmeric, which is very often added to flavoring extracts, and on a number of occasions it has been missed entirely owing to the fact that an insufficient amount of the extract had been evaporated upon the filter paper.

(10) It is recommended that the following methods be provisionally adopted:

METHODS FOR EXAMINATION OF LEMON AND ORANGE OILS.

1. SPECIFIC GRAVITY.

Determine the specific gravity by means of a pyknometer or a Sprengel tube at 15.6° C., as directed under "XIII. Wine," page 85, Bulletin 107, Revised.

2. INDEX OF REFRACTION.

Determine the index of refraction with any standard instrument, making the reading at 20° C.

3. ROTATION.

Determine the rotation at 20° C. with any standard instrument using a 50 mm tube and sodium light. The results should be stated in angular degrees on a 100 mm basis. If instruments having the sugar scale are used, the reading on orange oils is above the range of the scale, but readings may be obtained by the use of standard laevo reading quartz plates.

4. DETERMINATION OF CITRAL.

(a) *Kleber's method.*

Reagents.—Phenyl hydrazin: A 10 per cent solution of the purified chemical in absolute alcohol. A sufficiently pure product can be obtained by rectification of the commercial article, rejecting the first portions coming over which contain ammonia.

Hydrochloric acid: A half normal solution.

Manipulation.—Weigh 15 grams of the sample into a small glass stoppered flask; add 10 cc of the phenyl hydrazin solution. After allowing to stand for half an hour at room temperature, titrate with half-normal hydrochloric acid, using either methyl or ethyl orange as indicator. Titrate 10 cc of the phenyl hydrazin reagent in the same manner. The difference in cubic centimeters of half-normal acids between this titration and that of the sample, multiplied by the factor 0.076, gives the weight of citral in the sample.

If difficulty is experienced in detecting the end point of the reaction, carry the titration out until the solution is distinctly acid, transfer to a separatory funnel, and draw off the alcoholic portion. Wash the oil with water, adding the washings to the alcoholic solution, and titrate back with half-normal alkali, making the necessary corrections.

(b) *Hiltner's method.*

Proceed as directed under Lemon and Orange Extracts, weighing 2 grams of the oil, diluting to 100 cc, and using 2 cc of this solution for the comparison.

Hiltner prefers to use 5 grams of oil in the determination of lemon or orange oil by his method instead of 2 grams. In determining the total aldehydes and the citral in orange extracts, the fact previously stated must be borne in mind that this essential oil contains only part of its aldehydes as citral; indeed, there has been some discussion in the literature as to whether or not citral was present at all. However, a figure between 0.3 and 0.7 per cent is given by the Hiltner method on all the samples of genuine orange oil in the Washington laboratories. The fuchsin sulphite method will determine not only the citral but also the decylaldehyde of which from 1.5 to 2.5 per cent may be present. A figure above 0.7 per cent of citral by the Hiltner method is a very strong indication of the presence of either added citral or lemon oil.

5. DETERMINATION OF TOTAL ALDEHYDES.

Proceed as directed under Lemon and Orange Extracts, using from 2 to 5 grams of the sample in 100 cc aldehyde-free alcohol. This method should be used on orange oils the aldehydes of which are not determined by the other methods, although valuable information as to the content of added citral in the oil can be obtained by use of the Hiltner method.

6. DETERMINATION OF THE PHYSICAL CONSTANTS OF THE 10 PER CENT DISTILLATE (SCHIMMEL & CO.).

Place 50 cc of the sample in a 3-bulb Ladenburg flask in which the main bulb has a diameter of 6 cm and is of 200 cc capacity and which has the condensing bulbs of the following dimensions: 5.5 cm, 5 cm, 2.5 cm, and in which the distance from the bottom of the flask to the opening of the side arm is 20 cm. Distil the oil at the rate

of 2 cc per minute until 5 cc have been distilled. Determine the refractive index and rotation of this distillate as directed above.

7. DETECTION OF PINENE (CHACE).

Mix the 10 per cent distillate as obtained above with 5 cc of glacial acetic acid, cool the mixture thoroughly in a freezing bath, and add 10 cc of ethyl nitrite; then add slowly, with constant shaking, 2 cc of a mixture of 2 parts concentrated hydrochloric acid and 1 part of water which has been previously cooled. Keep this mixture in the freezing bath during this operation and allow it to remain therein for 15 minutes. Filter off the crystals formed, using vacuum and washing with strong alcohol. Return the filtrate and washings to the freezing bath and allow them to remain for 15 minutes. Filter off the crystals formed, using the original filter paper. Wash the two crops of crystals thoroughly with alcohol. Dry at room temperature and dissolve in the least possible amount of chloroform. Reprecipitate the nitroso-chlorid crystals with methyl alcohol and mount for examination under the microscope with olive oil. Pinene nitroso-chlorid crystals have irregular pyramidal ends while limonene nitroso-chlorid crystallizes in needle forms.

Drawings of these crystals are given in Circular 46, Bureau of Chemistry. Dr. L. D. Havenhill, of the University of Kansas, believes that the cooling of the filtrate to obtain a second crop of crystals is useless.

8. DETERMINATION OF ALCOHOL.

The amount of alcohol present in oils which have been used for the manufacture of terpeneless extracts may be approximately determined by washing repeatedly with small portions of saturated sodium chlorid solution and determining the alcohol in these washings in the usual way.

The methods for the determination of physical constants of orange and lemon oils are generally recognized as standard. No method has yet become standard for the determination of citral. The pinene method has been tried for several years both in the Washington laboratories and at New York, and there is no danger of detecting the traces of pinene which may occur naturally in lemon oils by the method. Certain results can not be obtained where less than 2 per cent of turpentine is present, while naturally occurring pinene is not in excess of 0.5 per cent. The presence of alcohol in oils is usually immediately noted owing to their low boiling point. In lemon oils the following reagent has been found of practical use for detecting its presence: 0.2 gram of cobalt nitrate, 0.4 gram of sulphocyanate of ammonia dissolved in 30 cc of water. Shake 5 cc of the oil with a few drops of this reagent, when alcohol will be indicated by the formation of a blue color. The method is not applicable to orange oils inasmuch as the alcohol bodies contained therein give the reaction.

In addition to these methods on the citrus fruit extracts, the associate referee believes that material good will ensue from the adoption of the following well-recognized methods for other extracts, no methods for which are included in the official or provisional methods at the present time.

(11) It is recommended that the following methods on almond extract be provisionally adopted:

ALMOND EXTRACT.

1. DETERMINATION OF ALCOHOL.

As almond extract does not usually contain other substances than oil of almonds and this oil only to the extent of 1 per cent, the alcohol can in most cases be calculated from the specific gravity of the extract. If the extract is high in solids, determine the alcohol as follows: Add 25 cc of the extract to 75 cc of a saturated solution of sodium chlorid in a separatory funnel and extract twice with separate 50 cc portions of petroleum ether (b. p. 40°–60° C.) Collect the petroleum ether extract in a second separatory funnel and wash twice with two separate 25 cc portions of saturated brine. Combine the original salt solution with the washings, add a little powdered pumice, and distil into a 100 cc flask. When almost 100 cc have been distilled, make up to mark at room temperature and determine alcohol from the specific gravity. If preferred, a 50 per cent solution of calcium chlorid may be used in place of the saturated brine in this method.

2. DETERMINATION OF BENZALDEHYDE (DENIS AND DUNBAR).

Reagent.—Add 1.5 cc of glacial acetic acid to 20 cc of water and mix with 1 cc of phenyl hydrazin.

Manipulation.—Measure out two portions of 10 cc each of the extract into 300 cc Erlenmeyer flasks and add 10 cc of the reagent to one flask and 15 cc to the other. Allow to stand in a dark place overnight, add 200 cc of distilled water and filter on a tared Gooch crucible provided with a thin coat of asbestos. Wash first with cold water, finally with 10 cc of 10 per cent alcohol, and dry for three hours in a vacuum oven at 70° C., or to constant weight over sulphuric acid. The weight of the precipitate multiplied by the factor 5.408, will give the weight of benzaldehyde in 100 cc of the sample. If duplicate determinations do not agree, repeat the operations using a larger quantity of the reagent.

3. DETECTION OF HYDROCYANIC ACID.

Add several drops of ferrous sulphate and a single drop of ferric chlorid to several cubic centimeters of the extract. Mix thoroughly, add sodium hydroxid, drop by drop, until no further precipitate forms and finally dilute hydrochloric acid in sufficient amount to dissolve the precipitate. In the presence of even small amounts of hydrocyanic acid, the blue coloration of Prussian blue will develop.

4. DETERMINATION OF HYDROCYANIC ACID IN THE ABSENCE OF CHLORIDS.

Measure into a small flask 25 cc of the extract and add 5 cc of freshly precipitated magnesium hydroxid (chlorin free). Titrate with tenth-normal silver nitrate solution using potassium chromate as an indicator. One cubic centimeter of tenth-normal silver nitrate is equal to 0.00268 gram hydrocyanic acid.

5. DETECTION OF NITROBENZOL.

Boil a few cubic centimeters of the extract with some zinc dust and acetic acid and filter. Add to the filtrate a drop of chloroform, make strongly alkaline with sodium hydroxid and heat. Where nitrobenzol was present in the original extract, the characteristic odor of phenyl isonitrile will develop.

The Denis-Dunbar method for the determination of benzaldehyde has received considerable attention at the various branch laboratories of the Bureau of Chemistry. The results obtained thereby are considered accurate, and the method is extremely simple in manipulation.

Another method has been in use in some of the laboratories of the bureau which was not received in time to be included in the original recommendations. It is by J. F. Darling, of the New York laboratory, and reads as follows:

Reagent.—An aqueous solution containing 5 grams of semicarbizone hydrochlorid and 7 grams of crystallized sodium acetate in 100 cc. About 21 cc of the reagent are equivalent to 1 gram of benzaldehyde.

Manipulation.—Measure 10 cc portions of the extract together with an excess of the reagent in a beaker, add approximately 75 cc of saturated salt solution and enough crystallized salt to saturate the mixture. Stir well, let stand for at least an hour, stirring at intervals. Filter on a tared Gooch crucible, wash with ice water, dry at 110° C. for one hour, cool, and weigh. The weight of the precipitate multiplied by 0.6502 is equal to the weight of benzaldehyde. For each 100 cc of wash water used, add 3.9 mg of benzaldehyde to the calculated amount. For assay of the oil of bitter almonds, make up a solution containing 2 grams of oil in 100 cc of 60 per cent alcohol and precipitate as above.

Mr. Pappe, of the Galveston laboratory, prefers this method to the Denis-Dunbar method, and it is also in use in the New York laboratory.

The methods recommended for the detection and determination of hydrocyanic acid are well established. It should be noted, however, that the determination must be made in chlorid-free solutions. The method for the detection of nitrobenzol has been long established in principle but has not been applied to flavoring extract work. It seems to be extremely delicate and no indications of a reaction have been observed with products of known purity.

(12) It is recommended that the following methods on spice extracts be provisionally adopted:

Cassia, Cinnamon, and Clove Extracts.

1. alcohol.

Determine as directed under Almond Extract.

2. oil (hortvet and west).

Transfer 10 cc of the extract to a separatory funnel, add 30 cc of water, acidify with 1 cc of 1:1 hydrochloric acid and extract three times with ether, using not less than 100 cc altogether. Wash the ether solution twice with water and in the case of cinnamon extract dry by shaking with a small amount of granulated calcium chlorid. Transfer to a wide mouth tared weighing bottle and evaporate the ether as rapidly as possible on a boiling water bath, rotating the liquid upon the sides of the flask in order to rid the residual oil of traces of ether. Weigh the residue and divide the weight by the specific gravity of the oil in order to obtain the volume—cassia by 1.05, cinnamon by 1.03, clove by 1.055. In the case of clove oil, allow the weighing bottle to remain upon the balance until the usual film of moisture has evaporated; the time of weighing should not be delayed over three minutes, however.

Determine the refractive index of the residual oils at 20° C. The refractive index of cassia oil at this temperature is from 1.585 to 1.60, of cinnamon from 1.590 to 1.599, and of clove from 1.560 to 1.565.

Dissolve a drop of the oil in several drops of alcohol, and add a drop of ferric chlorid solution. Cassia oil develops a green, cinnamon a brown, and clove a deep blue coloration.

The Hortvet and West method recommended for cassia, cinnamon, and clove extracts is probably the only method available for their accurate determination. Much individual judgment must be brought into play in evaporating the ether from the oils themselves as a marked loss will take place if the evaporation is carried too far.

(13) It is recommended that the following methods be provisionally adopted:

Ginger Extract.

1. alcohol.

Determine as directed under Vanilla Extract.

2. solids.

Evaporate 10 cc of the extract nearly to dryness on a water bath, dry for two hours in a water oven and weigh.

3. test for ginger (seeker).

Dilute 10 cc of the extract to 30 cc, evaporate off 20 cc, decant into separatory funnel and extract with an equal volume of ether. Evaporate the ether spontaneously in a porcelain dish and to the residue add 5 cc of 75 per cent sulphuric acid and about 5 mg of vanillin. Allow to stand for 15 minutes and add an equal volume of water; in the presence of ginger extract an azure blue color develops.

4. tests for capsicum (la wall, nelson).

Dealcoholize 20 cc of the extract as directed under vanilla, extract with ether and divide the ether extract into two parts. Transfer one part to a test tube, evaporate to dryness and add 5 cc of alcoholic potash, heating for half an hour in a boiling water bath under a reflux cooler. Evaporate to dryness, take up the residue in water and extract with ether. Evaporate the ether to dryness and test the residue by taste. To the second part of the original ether extract add 10 cc of alcoholic potash, evaporate to dryness in a porcelain dish and add 0.1 gram of manganese dioxid. Dilute with 10 cc of water, heat for 20 minutes on a water bath, cool, and extract with petroleum ether. Evaporate the petroleum ether, heat for five minutes to expel volatile oils and test for capsicum by taste.

The methods recommended for ginger are all that seem available at the present time. The study of ginger oil, and consequently of the extract, are incomplete at the present time, and as there is no method available for the determination of the active principle of ginger extract reliance must be placed very largely on the determination of the solid matter which they contain, making correction for any sugar present, which is not as a rule added to this class of extracts. The tests for capsicum have been under trial for some time and are believed to be sufficiently reliable for provisional adoption.

(14) It is recommended that the following methods be provisionally adopted:

NUTMEG AND WINTERGREEN EXTRACTS.

1. ALCOHOL.

Determine as directed under Almond Extract.

2. ESSENTIAL OIL.

Use the method by precipitation described under lemon and orange extracts, making no correction in the volume of the precipitated oil. As nutmeg and wintergreen oils are of a greater specific gravity than water, it will be necessary to add saturated salt solution in the case of nutmeg and sulphuric acid (1:1) in the case of wintergreen oils in order to bring them into the neck of the measuring flask.

(15) It is recommended that the following methods be provisionally adopted:

PEPPERMINT EXTRACT.

(1) ALCOHOL.

Determine as directed under Almond Extract.

(2) PEPPERMINT OIL.

Pipette 10 cc of the extract into a Babcock milk bottle and add 25 cc of cold water, 1 cc of cold hydrochloric acid, specific gravity of 1.2, and 0.5 cc of chloroform. Close the mouth of the bottle with the thumb and shake vigorously for not less than one minute. Whirl the bottle in a centrifuge for two minutes and remove all but 3 or 4 cc of the clear supernatant liquid by means of a glass tube of small bore and aspiration. To the residue add 1 cc of ether, agitate thoroughly, plunge the bottle to the neck in boiling water, holding at a slight angle, and rotate in the bath exactly one minute. Cool, fill the bottle to the neck with water at room temperature, centrifuge, and read the volume of the separated oil from the top of the meniscus and multiply the reading by 2 to obtain the per cent of oil by volume.

CONCLUSIONS.

It is fully believed that the provisional adoption of these methods by the association will be a material help to the analyst witnesses who testify in both State and Federal cases, in which great stress is very often laid upon the fact as to whether or not the method used has been adopted by this association. In cases before the Board of Food and Drug Inspection, objection has been raised when the analyst witness varied even so far from the directions given in the official method as to weigh the extract instead of measuring, as described in the method, and it would seem that the necessity for the accurate and clear statement of methods for all food products is rapidly increasing. Methods can not be adopted until they have been tested, and therefore, only those methods which have had some trial are recommended at this time for provisional adoption.

GINGER EXTRACT.

By JOHN PHILLIPS STREET and C. B. MORISON.

Standard ginger extract is "the flavoring extract prepared from ginger and contains in each one hundred (100) cubic centimeters, the alcohol-soluble matters from not less than twenty (20) grams of ginger." This standard is also the same as that required by the U. S. Pharmacopœia for medicinal tincture of ginger.

In determining the strength of a ginger extract in comparison with the standard it is necessary to know how much alcohol-soluble matter powdered ginger root will yield. The kind of ginger used will have an important bearing on the amount of alcohol extractive. Winton, Ogden, and Mitchell [1] and Reich [2] have made very complete examinations of authentic samples of ginger. The average alcohol-soluble matter determined by them in using the same method was as follows:

[1] Conn. Agr. Exper. Sta. Rept., 1898, 203. [2] Zts. Nahr. Genussm., 1907, 14: 549.

Determination of alcohol-soluble material in an authentic ginger sample.

Kind of ginger.	Winton.	Reich.
	Per cent.	*Per cent.*
Jamaica	4.97	.....
Cochin	5.00	3.96
Japan	5.02	5.80
African	6.34	6.64
Calcutta	4.33	4.36
All samples	5.18	5.19

The individual samples showed considerable variation in the hands of both analysts, Winton's ranging from 3.63 to 6.58 per cent and Reich's from 3.24 to 8.05 per cent, the maxima in both cases being secured from African ginger. While these are wide variations, we are chiefly concerned with Jamaica and African ginger, the more commonly used varieties, and in these the variations are somewhat smaller, from 4.04 to 8.05 per cent. Based on these figures 100 cc of standard extract of ginger should contain from 0.80 to 1.60 grams of alcohol-soluble solids, or, based on a specific gravity of 0.820, from 0.97 to 1.94 per cent.

Two samples of tincture of ginger were prepared in the Connecticut station laboratory, following the U. S. Pharmacopœia directions, which should give a preparation of the same strength as the standard extract. The analyses are given below:

Analysis of a U. S. Pharmacopœia tincture of ginger prepared in the laboratory.

Determinations.	Jamaica.	African.
Specific gravity (15.6° C.)	0.8198	0.8222
Alcohol by volume	94.63	93.21
Total solids	1.43	1.81
Solids soluble in 95 per cent alcohol	1.42	1.81
Solids soluble in cold water	0.21	0.16

The most striking characteristic of these tinctures is the high alcohol-solubility of the solids; it is also noticeable that only a small proportion of the material soluble in 95 per cent alcohol is likewise soluble in cold water. From these analyses and those of Winton and Reich it would seem that a properly prepared extract of ginger should show a specific gravity of about 0.820, and should contain at least 93 per cent of alcohol by volume, from 1 to 2 per cent of solids, practically all of which should be soluble in 95 per cent alcohol, and not over 15 per cent soluble in cold water.

The most common form of adulteration of this extract is the use of alcohol of low strength. Unlike most flavoring extracts, in ginger extract a weak alcohol possesses a higher extractive power than a strong one, for ginger root contains much more (in Jamaica ginger three times as much) matter soluble in water than in alcohol. This increased extractive power, however, adds nothing to the value of the extract, as the valuable principles of the root, the essential oil and the oleoresins, have but a low solubility in dilute alcohol. It is apparent that a simple determination of solids will show little as to the quality of the extract, not only because a weak alcohol may have been used but also because sugar or glycerol, or both, are frequently used to fortify weak extracts.

The lead number, similar to that suggested by Winton for maple syrup and later for vanilla extract, was determined in a number of the samples. In the samples made in the laboratory lead numbers of 0.23 and 0.29 were obtained, while in the samples classed as pure 0.24, 0.28, and 0.36 were secured. On the other hand, the compound and adulterated extracts showed similarly low lead numbers in the great majority of cases, although in two samples 0.70 and 0.73 were secured. In one of these molasses was declared on the label. It does not appear that this determination

has much value in judging a ginger extract, although a high number points with reasonable certainty to the presence of molasses.

To study further the effect of alcohols of different strengths on the amount of total solids and their solubility, two other tinctures were prepared, using alcohol of 60 and 20 per cent by volume. The data obtained are given in the table in comparison with those obtained when 95 per cent alcohol was used.

Determinations of total and soluble solids in tinctures prepared with different strengths of alcohol.

Determinations.	95 per cent alcohol.	60 per cent alcohol.	20 per cent alcohol.
Total solids	1.43	1.91	2.59
Solids soluble in alcohol	1.42	1.16	0.30
Solids soluble in cold water	0.21	1.23	2.09

These results are quite what would be expected. As the alcoholic strength decreases the amount of solids increases, and a greater proportion is soluble in water and a less in alcohol. It is evident, therefore, that the high solids found in certain extracts, and the abnormally high proportion of these solids soluble in water, may in certain cases be due quite as much, if not entirely, to the weak alcohol employed as to added sugar or glycerol.

Thirty-four samples sold as flavoring extracts and 14 sold as tincture of ginger were examined, but only the full analyses of certain ones which are typical and a general summary of all the samples, will be given. Seven of the flavoring extracts are classed as of standard composition, 7 as legally labeled compounds, and 20 as below standard or adulterated. Of the tinctures 12 are of standard quality.

The 7 standard extracts and the 12 standard tinctures ranged in specific gravity from 0.8218 to 0.8366, average, 0.8278; alcohol from 90.52 to 96.18, average, 93.50; total solids from 0.94 to 1.85, average, 1.37; solids soluble in alcohol from 0.94 to 1.72; and solids soluble in water from 0.08 to 0.47. From 89 to 100 per cent of the solids were soluble in alcohol, and from 6 to 38 per cent in water.

The compound extracts were made from dilute alcohol and contained sugar, molasses, glycerol, caramel or capsicum, alone or in combination. They ranged in specific gravity from 0.9242 to 0.9948, alcohol from 35.20 to 56.07, total solids from 0.49 to 10.14, solids soluble in alcohol from 0.42 to 2.86, and solids soluble in water from 0.22 to 9.72. From 8 to 100 per cent of the solids was soluble in alcohol, and from 25 to 96 per cent in water.

The extracts below standard or adulterated were so classed either because of low-alcohol percentages or because of an excess of water-soluble solids. In certain cases these solids were derived only from the ginger root itself, while in others they were due, at least in part, to added glycerol, sugar, or molasses. Certain of the weakest extracts were labeled "concentrated." The samples ranged in specific gravity from 0.8284 to 0.9900, alcohol from 21.35 to 95.00, total solids from 0.52 to 9.90, solids soluble in alcohol from 0.21 to 4.50, and solids soluble in water from 0.07 to 9.12. From 10 to 100 per cent of the solids were soluble in alcohol, and from 13 to 92 per cent in water.

In the following tabulation are given the average analyses of the standard extracts and tinctures, certain typical compound and adulterated extracts, two tinctures below standard, and the four tinctures made in the laboratory with 95, 60, and 20 per cent alcohol.

Analytical data on ginger extracts and tinctures of different qualities.

Preparation.	Specific gravity at 15.6° C.	Alcohol by volume.	Solid matter.			Per cent of total solids soluble—		Remarks.
			Total.	Soluble in alcohol.	Soluble in water.	In alcohol.	In water.	
Average 7 standard extracts	0.8291	93.78	1.38	1.33	0.28	97	20	
Average 12 standard tinctures	.8271	93.33	1.36	1.30	.23	96	17	
Laboratory sample:								
African, 95 per cent alcohol.	.8222	93.21	1.81	1.81	.16	100	9	
Jamaica, 95 per cent alcohol.	.8198	94.63	1.43	1.42	.21	99	15	
Jamaica, 60 per cent alcohol.	.....	.....	1.91	1.16	1.23	61	64	
Jamaica, 20 per cent alcohol.	.....	.....	2.59	.30	2.09	12	81	
Compound:								
A	.9584	48.55	6.45	1.20	6.08	19	94	Contains sugar, caramel, and water.
B	.9242	56.07	.87	.87	.22	100	25	Contains water.
C	.9948	38.07	10.14	.86	9.72	8	96	Contains molasses and water.
D	.9588	37.28	.49	.42	.41	86	84	Contains capsicum and water.
E	.9557	39.35	1.18	.54	1.01	46	86	Contains oleoresin ginger, oleoresin capsicum, essence oil ginger, caramel, and water.
Adulterated:								
F	.9184	59.88	2.17	1.12	1.51	52	70	Weak alcohol extract.
G	.9325	46.96	.36	.36	.14	100	39	Exhausted ginger used (?).
H	.9567	54.28	9.90	1.39	9.12	14	92	Contains sugar and water.
I	.9900	21.35	4.29	.63	3.57	15	83	Do.
J	.9617	34.90	.59	.56	.58	95	98	Contains water.
K	.9657	35.93	2.17	.21	1.97	10	91	Contains water and caramel.
Tinctures below standard:								
L	.8359	93.89	2.23	1.23	.68	55	30	Alcohol solubility of solids too low.
M	.8587	85.34	2.59	1.84	1.12	71	43	Do.

The methods used to secure these results are briefly as follows:

Alcohol.—As the volatile oil was found to interfere seriously in the determination of the high percentages of alcohol, 15 grams of the extract were diluted with water to 100 cc in a 200 cc Erlenmeyer flask, then 2.5 grams of magnesium carbonate were added, shaken thoroughly, and filtered through a small plaited filter, the alcohol being distilled from 75 cc of the filtrate.

Total solids.—Weigh from 5 to 10 grams of extract into a tared flat-bottomed dish and evaporate to apparent dryness at a moderate temperature (there is danger of loss by spurting in samples containing high percentages of alcohol). Dry to constant weight in drying oven at the temperature of boiling water.

Solids soluble in alcohol.—Add 15 cc of 95 per cent alcohol to the dried residue obtained as above. Stir thoroughly with a glass rod and allow to stand for one hour. Wash into a 50 cc flask with 95 per cent alcohol and make up to the mark. Filter the solution through a dry plaited filter, evaporate an aliquot of 25 cc, and weigh as for total solids, taking the same precautions as before to insure a slow evaporation of the alcohol.

Solids soluble in water.—Add 15 to 20 cc of water at room temperature to the residue obtained in total solids determination. Stir with glass rod at frequent intervals during three hours. Because of the gummy character of many residues it is sometimes difficult to secure proper contact with the solvent. Wash into a 50 cc flask with water and make up to the mark. Filter the solution through a dry plaited filter, and evaporate an aliquot of 25 cc and dry to constant weight in a water oven.

REPORT ON SPICES.

By A. F. Seeker, *Associate Referee.*

Preliminary Work.

Continuing the work of last year on the detection of added oil in paprika (Proceedings of 1909, Bulletin 132, p. 112) the referee has secured, through Mr. R. E. Doolittle, from the firm of Francisco Flores, of Murcia, Spain, four samples of whole Spanish peppers which are typical of the different kinds ground to prepare the Spanish red pepper of commerce. These were ground by the referee after the stems had been separated and rejected. To ascertain if the ether extracts or iodin numbers of the ether extracts of all these samples were normal and comparable to those obtained by Doolittle and Ogden,[1] they were examined by D. L. Weatherhead, who employed the method detailed in this report. The values were found to be normal, and from the data at the present time available there would be no hesitation in pronouncing them free from added olive oil.

The description of the four samples is as follows:

(1) *Cascara vieja.*—Crop of 1908, pods slit open and dried in the air. This sample was in very poor condition, being rather mouldy and badly infested with weevils. The shells had lost much of their color and when ground yielded a product of very inferior grade. A large proportion of the seeds had evidently been lost during the drying process through the slit in the pods. Stems (42 grams) 10.7 per cent, seeds (90 grams) 23 per cent, and shells (260 grams) 66.3 per cent.

(2) *Noras vieja.*—Crop of 1908, pods dried whole. When ground it yielded a dull, dark red product. Stems (30 grams) 11.2 per cent, seeds (90 grams) 33.6 per cent, and shells (148 grams) 55.2 per cent.

(3) *Cascara nueva.*—Crop of 1909, pods slit open and dried in the air. Slightly infested with weevils. Yielded a bright light-red powder. Stems (10 grams) 3.1 per cent, seeds (84 grams) 26.3 per cent, and shells (225 grams) 70.6 per cent.

(4) *Noras nueva.*—Crop of 1909, pods dried whole. Yielded a bright, dark-red powder. Stems (30 grams) 12.9 per cent, seeds (68 grams) 29.2 per cent, and shells (135 grams) 57.9 per cent.

Determinations on the four samples.

Determinations.	No. 1.	No. 2.	No. 3.	No. 4.
Ether extract (per cent)	9.01	10.32	8.86	9.49
Iodin number	130.40	129.30	137.50	137.50

Owing to the greater proportion of seeds in the "Noras" grades which are dried with unopened pods, the ether extract is higher than in those dried after being opened and from which some of the seeds have been lost.

The iodin number of the ether extract is appreciably lower in the "Vieja" grades, but whether this is because they are a year older than the "Nueva" or whether this was characteristic of that year's crop can not now be determined with certainty. It seems possible that a slow oxidation of the paprika oil can take place upon mere aging of the product, and experiments to determine this point are now being conducted by the referee.

To test further the reliability of the iodin number of the ether extract for detecting the presence of olive oil in paprika four samples of known character, ground and prepared by the referee, were submitted to eleven collaborators for examination by a prescribed method. The procedure selected was the one designated as Method II in the report of 1909, with some modifications suggested by the collaborators as a result of last year's work. The method for obtaining the ether extract is somewhat similar to that for determining alcohol extract in spices as employed by Winton which is now provisional (Bul. 107, Rev., p. 163).

[1] J. Amer. Chem. Soc., 1908, **30**: 1481.

Statement of the Method.

Spread 5 grams of paprika on a watch crystal and dry over sulphuric acid for at least 12 hours. Measure 250 cc of anhydrous alcohol-free ether, prepared as directed on page 39 of Bulletin 107, Revised, into a graduated flask on which the mark is situated near the lower end of the neck, and brush the paprika into it. Place a mark on the neck of the flask at the point where the meniscus is, and allow to stand for one hour, shaking at 20 minute intervals during that time. Bring the meniscus back to the mark placed upon the neck, either by cooling the flask and contents if the level has risen, or by adding absolute ether if it has fallen. Let the solid particles settle, pipette off 100 cc of the supernatant liquid, and filter this through an 11 cm closely woven paper into a tared, air dry 250 cc Erlenmeyer flask (glass stoppered) that has been counterpoised against a similar flask. Wash the paper with a little absolute ether, and then distil off the solvent, removing the flask from the bath as soon as the ether ceases to come over. Lay the flask on its side in a water oven and heat for 30 minutes; cool the open flask for at least 30 minutes in the air and weigh. Repeat this heating and weighing until the weight is constant to within 1 mg, two heatings usually being sufficient. Note the per cent of ether extract obtained.

Dissolve the ether extract in the flask with 10 cc of chloroform, and when solution is complete add 30 cc of Hanus solution, following the method on page 137, Bulletin 107, Revised, and allowing 30 minutes for the halogen absorption. Note the iodin number of the ether extract. A second aliquot of 100 cc, measured out immediately after the first, may be taken from the ether extract in the graduated flask in order to run a duplicate determination of the iodin number. If it is found necessary to heat the ether extract longer than one and one-half hours to obtain constant weight, or if the extract is decolorized on heating, the determination should be rejected and a new one made using freshly purified ether. The iodin number of pure paprika extract obtained by this method should not be less than 125.

Discussion of Details of Method.

Considering the various steps of the method in their order:

Five grams of material are taken for the reason that the 100 cc of ether solution finally used as an aliquot of 250 cc contains the proper amount of extract for rapid drying and for the determination of the iodin number.

Drying over sulphuric acid for 12 hours requires no special apparatus, and removes whatever moisture is likely to influence adversely the composition of the ether extract.

The use of absolute ether, free from moisture and alcohol, is an essential requirement deserving special mention owing to the fact that a solvent containing those substances yields an extract of different composition and lower iodin number than one obtained by the use of pure absolute ether. As an example of this, A. E. Taylor, one of the collaborators, has furnished a set of results on the four samples sent out this year which were obtained by the use of hydrous and anhydrous ether:

Results obtained on referee's samples[1] *using hydrous and anhydrous ether.*

Determinations.	Sample C.	Sample D.	Sample E.	Sample F.
Hydrous ether:				
Ether extract (per cent)	9.85	11.39	14.67	16.09
Iodin number	115.4	123.2	102.4	105.8
Anhydrous ether:				
Ether extract (per cent)	9.20	10.97	14.09	15.41
Iodin number	123.7	129.0	108.9	113.1

[1] See page 80 for description of samples.

On comparing the results obtained by this analyst using the perfectly dry absolute ether and using ether containing moisture the importance of this point is obvious.

The 250 cc flask is filled with ether before introducing the paprika, rather than the reverse, so that later, when taking an aliquot of 100 cc it will represent a true fraction

($\frac{100}{250}$) of the original material and not be subject to the error that would arise from neglecting the volume occupied by the insoluble portion of the paprika. A mark is placed on the neck of the flask so that any change in volume due to evaporation or temperature may be noted and corrected before drawing the aliquot.

One hour's contact of material and solvent was selected because it allows rapid work, extracts from 90 to 95 per cent as much as the official method, and gives almost exactly the same results as those obtained by the procedure of Doolittle and Ogden,[1] making available all their work on authentic samples in drawing comparisons and interpreting results.

The aliquot is taken directly from the flask with a pipette and filtered afterwards because the referee and many of the collaborators have found that the ordinary procedure of filtering first and taking the aliquot from the filtrate is attended with serious losses from evaporation, the extent of these losses being dependent upon such circumstances as temperature, air currents, rapidity of filtration, etc. A pipette can readily be used for taking the aliquot, if instead of sucking the ether solution into it the liquid be forced in by an arrangement similiar to that of a wash bottle, the pipette taking the place of the usual outlet tube.

The use of a 250 cc Erlenmeyer flask in which to weigh the ether extract allows an iodin number determination to be conducted upon it without transferring, saving time and possible loss of material. To weigh such a large glass vessel accurately and to provide for changes in weight resulting from changes in the condition of the atmosphere it is of course necessary to employ a counterpoise of the same size and material as the method prescribes.

The flasks are cooled in the air rather than in a desiccator for the reason that owing to their large surface and the variable absorption of moisture resulting under different atmospheric conditions weighing is found more accurate when they are air dry. The interval of 30 minutes between the time of removal from the water oven and the weighing has been found necessary in order to avoid erratic weighings, the reason being conjectured to be due to the variable absorption of moisture from the atmosphere by the glass surface before equilibrium is reached.

The directions for heating at 30-minute intervals in a water oven are given because heating at higher temperatures or for prolonged periods causes oxidation of the extract and consequent diminution of the iodin number. This is shown by the following values (the work of D. L. Weatherhead under the direction of the referee) which were obtained by extracting an authentic sample of paprika with ether, filtering the ether solution, taking four equal measured portions of it, distilling off the ether, and drying the resulting extract as described in the table. The first line shows the values obtained when operating as prescribed by the method.

Results obtained by varying the conditions of drying (Weatherhead).

Sample.	Character of drying.	Ether extract.	Ether extract.	Iodin number of ether extract.
		Grams.	*Per cent.*	
1	Usual	0.2123	10.62	136.5
2	8 hours at 100° C	.2159	10.80	102.1
3	4 hours at 110° C	.2162	10.81	71.5
4	8 hours at 110° C	.2149	10.75	58.2
5	14 days at room temperature	.2124	10.62	132.0

[1] J. Amer. Chem. Soc., 1908, 30: 1481.

Laying the flask on its side in the water oven facilitates the escape of ether vapor.

The reasons for each step have been given in full in order to show that the apparent multiplication of details in the method are necessary in order to secure uniformity in manipulation and to obtain comparable results among different analysts. It should be recalled that there are two arbitrary procedures in the method, first that of obtaining the ether extract, and second the iodin number of this extract. Knowing as we do that there is not always such concordance as is desirable among different analysts in reporting the iodin number of the same identical substance, many more possibilities for disagreement are presented if that substance is allowed to be of variable composition. It is held, therefore, that the directions should be as explicit as possible.

Cooperative Results.

Eleven analysts have reported results obtained by the proposed method on four samples, furnished by the referee, which were ground and prepared by him. The nature of these samples was as follows:

C. Spanish red pepper from which the stems were separated, the shells and all the seeds being ground together.

D. Hungarian paprika from which the stems were separated, the shells and all the seeds being ground together.

E. Sample C with which 5 per cent of olive oil was thoroughly incorporated.

F. Sample D with which 5 per cent of olive oil was thoroughly incorporated.

The collaborators from whom reports were received are named in the following list, the numbers indicating the position of their results on the table:

(1) H. S. Bailey, Washington, D. C. (2) C. S. Brinton, Philadelphia, Pa. (3) A. T. Collins, Philadelphia, Pa. (4) C. O. Dodge, Washington, D. C. (5) A. W. Hansen, Chicago, Ill. (6) C. I. Lott, Buffalo, N. Y. (7) F. D. Merrill, San Francisco, Cal. (8) H. E. Sindall, Philadelphia, Pa. (9) A. E. Taylor, Savannah, Ga. (10) D. L. Weatherhead, New York, N. Y. (11) C. P. Wilson, Washington, D. C.

Cooperative results on paprikas by the proposed method.

Analyst.	Sample C.		Sample D.		Sample E.		Sample F.	
	Ether extract.	Iodin number.	Ether extract.	Iodin number.	Ether extract.	Iodin number.	Ether extract.	Iodin number.
	Per cent.		*Per cent.*		*Per cent.*		*Per cent.*	
1	9.35	125.7	10.93	134.4	13.50	112.7	15.15	118.2
2	9.85	127.8	11.50	132.1	14.40	111.9	15.78	116.9
	9.85	128.4	11.39	132.6	14.38	.....	15.85	116.1
3	9.85	125.1	11.40	129.4	14.30	109.3	15.71	114.9
	9.85	125.1	11.40	129.3	14.20	110.0	15.71	114.9
4	9.65	127.1	11.25	132.8	14.07	112.3	15.51	116.4
5	9.97	125.4	11.47	130.5	14.41	110.6	16.04	114.9
6	10.21	121.2	11.67	130.7	14.60	104.9	16.43	111.5
	9.99	123.9	11.50	130.4	14.72	106.5	15.84	113.4
	9.84	119.8	11.44	128.7	14.34	105.4	15.88	113.6
	9.93	125.5	11.49	131.4	14.48	106.8	.....	.....
7	8.55	123.2	10.50	130.1	13.45	108.4	14.47	116.0
8	11.06	127.1	12.05	133.1	15.25	109.6	15.54	116.7
	11.16	127.2	12.03	132.7	15.35	110.1	15.51	116.5
9	9.20	123.6	10.97	129.1	14.40	109.5	15.77	113.8
	.....	123.9	.....	128.9	13.77	108.2	15.05	112.3
10	9.62	129.0	11.17	134.1	14.29	112.2	15.52	118.1
	9.53	128.8	11.15	133.7	14.11	113.1	15.55	114.4
11	9.98	122.4	11.55	129.8	14.53	105.8	16.01	112.4
	.....	119.7	.....	129.2	.....	104.8	.....	112.4
Average	10.02	125.0	11.38	131.2	14.34	109.1	15.63	114.9

Comments by the Collaborators.

Mr. Bailey experienced considerable difficulty in getting the extracts dried to constant weight and feared that his ether contained some moisture, though it had stood over sodium for some months and appeared to be in good condition. It left a small amount of nonvolatile residue for which corrections were made.

Mr. Brinton: The figures indicate, to my mind, that this method is very satisfactory and that closely agreeing duplicates can be obtained on both the ether extract and the iodin number. I have one criticism to make of the method but do not see at present how it can be overcome. By transferring the sample to a watch glass a certain amount of oil remains attached to the watch glass and can not be washed or rinsed off because ether has already been used in the flask, consequently the total ether extract is slightly decreased, and the error is greater of course in samples containing large quantities of oil. Unoiled samples would leave practically no stain on the watch glass.

Mr. Collins considers the results much more satisfactory than last year's, and attributes this to two causes, the device of taking an aliquot of the ether solution with a pipette, and second, a refined method of reading his burettes, for which purpose he employed a small telescope permitting estimations of 0.01 cc.

Mr. Sindall: I followed the method exactly and consider it to be nearer correct than any other I know of at this time. The method of filling the pipette as shown in the photograph sent is a great improvement over the old way.

Summary.

Reviewing the results reported this year, the following summary has been prepared in which two comparisons are made, one based on the individual results reported by each analyst and the other on the average for each sample as reported by each collaborating chemist. The former statement does not furnish a fair estimate of the actual agreement, for the reason that many of the values excluded were reported by the same analysts, some of whom gave results of duplicate and quadruplicate determinations, while many others reported only single determinations. The limit of error given is the amount of plus or minus variation allowed from the average of all the results reported.

Comparative summary of individual and of average results.

Limit of error.	Total number of analyses.	Number in agreement.	Number excluded.	Per cent of agreement.
Individual results:				
Ether extract (per cent)—				
0.25	73	47	26	64
0.40	73	55	18	75
Iodin number:				
3 units	78	68	10	87
Average results:				
Ether extract (per cent)—				
0.25	44	27	17	61
0.40	44	32	12	73
Iodin number—				
3 units	44	40	4	91

Recommendations.

Taking into consideration that this method was used for the first time by many of the collaborators who were unfamiliar with its manipulative details, a very creditable concordance was obtained, and as the procedure has also been used for the past year with entire satisfaction at the New York Food and Drug Inspection Laboratory in the routine examination of commercial paprika, the referee feels justified in recommending that it be made a provisional method to be designated "Method for the detection of olive oil in paprika."

It is also recommended that a further study be made of the chemical characteristics of paprika extract with a view to detecting foreign oils other than olive oil, and also the effect of drying the ether extract in vacuo or in an atmosphere of hydrogen. In this connection the referee submits the following results obtained by Dr. William Szigeti, of Brasso, Hungary, which were communicated to him through the Austro-Hungarian consul general at New York City:

Specific gravity (15.5° C.)	0.9136–0.9318
Hehner value	90.72
Reichert-Meissl value	5.2
Saponification value	184.64–189.68
Iodin number	112.03–116.24
Acetyl value	63.95– 66.23
Refractive index (15° C.)	1.489– 1.490
Melting point of the fatty acids	22.2°
Average molecular weight of the fatty acids	282
Iodin number of the fatty acids	131.19–132.43
Average molecular weight of the solid fatty acids	266

From Weatherhead's data on drying paprika extract as given in the table on page 82 of this report it would seem very important to know how Dr. Szigeti dried his extracts, for if no precautions were taken to avoid oxidation his iodin numbers are undoubtedly too low. A consideration of his figures would seem to indicate that the refractive index and the acetyl value would best serve to detect the presence of foreign oils.

QUICK METHOD FOR DETERMINING ETHER EXTRACT IN DRY POWDERED SUBSTANCES: COCOA, COFFEE, SPICES, ETC.

By A. E. Leach and R. S. Hiltner.

The official method for ether extract in these substances requires for the extraction alone 20 hours in some form of continuous extractor. It is often the case that it is undesirable to let this apparatus operate unattended overnight, but to shut it off other than during working hours will necessitate three working days in the practice of extraction, not to mention the time used in connecting and sealing the apparatus, which is by no means a trivial consideration.

It was to obviate this difficulty that the following simplified method of procedure was tried for making quick ether extract determinations, the process of extraction alone consuming only a few minutes for each sample. Indeed, if a sample or a series of samples is weighed out late in the afternoon, final weighings of the ether extract may usually be made the first thing the following morning, and the results agree very satisfactorily with those obtained by the official method.

Weigh 2 grams of the substance upon a watch glass and transfer to a small beaker of at least 100 cc capacity. Treat with about 20 cc of ordinary ether and shake continuously by rotating the beaker, taking care to avoid overflow and loss. Let stand for a few minutes, then transfer rapidly to a quick-acting filter in a funnel placed in the neck of a tared 100 cc Erlenmeyer flask. Effect a quick transfer of contents of beaker to filter by the aid of a stream of ether from a wash bottle. Wash the filter with additional ether from the wash bottle till the filtrate amounts to about 75 cc, taking care to avoid the formation of a layer of ether extract at the top of the filter paper. Place the open flask with the ether extract in a warm place where the temperature registers from 40° C. to 50° C., and allow to remain until all of the ether has evaporated, usually from 17 to 18 hours. Then cool and weigh for total ether extract. Ordinary ether has been used instead of the anhydrous variety, with equally good results, in the classes of products thus far tried.

The main uncertainty lies not in a complete extraction, for that seems assured in the case of fine powders, but in the complete removal of the ether without driving off any of the essential oil, when the latter is present. Generally the appearance and odor of the residue will indicate when all the ether has evaporated, which in most cases occurs

within the period specified above. Occasionally, as in ginger, the consistency of the residue indicates that a longer period of drying is necessary, it being assumed that at a temperature not exceeding 45° C. no appreciable loss occurs in the volatile oil of spices, etc., especially in an Erlenmeyer flask.

The accuracy of the official method in like manner depends on the certainty with which the ether is itself evaporated without loss of volatile oil. This in turn depends much on the size and shape of the tared capsule or flask from which the ether is finally allowed to evaporate, as well as on other conditions, and is by no means satisfactorily worked out. This point, especially, should be further studied. As to time of actual extraction in the use of the official method with continuous extraction, there seems to be little doubt that, in spices and similar dry powders, all the ether-soluble matter is removed very soon after the apparatus is started. Thus much valuable time may be wasted by prolonged extraction. This is by no means true, however, of many substances that concern the analyst, and the matter should be investigated.

It is not intended that the proposed method should be substituted for the official method for ether extract; at any rate not until it has been thoroughly tried. The results so far obtained, however, would indicate that it offers a simple, rapid, and reliable means by which the food analyst may separate the genuine from the adulterated samples. The following are a few comparative results obtained by the two methods:

Comparison of results by the official and the proposed method.

Substance.	Ether extract.		Substance.	Ether extract.	
	Official method.	Proposed method.		Official method.	Proposed method.
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
Black pepper	8.76	8.33	Cinnamon	3.95	3.98
Cloves	22.09	22.03	Ginger	5.20	5.18
Chocolate	12.43	12.28	Cayenne	18.88	18.33
Mustard	28.43	28.55			

REPORT ON BAKING POWDERS.

By Edmund Clark, *Associate Referee.*

Owing largely to the generally satisfactory condition of the official methods for the analysis of baking powder, so far as the associate referee is aware, no collaborative work was undertaken. A slight but important change in the official methods has been recommended to the committee in regard to the use of sulphuric acid instead of hydrochloric acid in the determination of carbon dioxid.

Although no collaborative work on methods was done during the year, the referee would like to call to the attention of the association a few observations along the lines suggested in the report on this subject last year, namely, the examination of baking-powder ingredients for injurious and poisonous substances, and the fraudulent use of fillers in commercial acid calcium phosphate. Among the dangerous impurities which have been found in calcium acid phosphate is fluorin, probably present as calcium fluorid. Fluorin has been approximately determined in four official samples by A. G. Woodman, using the method described by him in the Journal of the American Chemical Society, October, 1906. Woodman found approximately 0.05, 0.04, 0.2, and 0.05 per cent of fluorin in these four samples of acid phosphate. It has long been recognized that compounds of fluorin are actively poisonous to animals even in minute quantities, and it seems as though the question of degree of toxicity and the maximum amount of fluorin to be permitted in foods must soon be settled, for the delicacy of

the test for its detection is such that traces of fluorin may be found in almost all natural products.

With 0.2 per cent of fluorin in acid calcium phosphate and 40 per cent of this acid ingredient in baking powder, by using the commercial formula of one teaspoonful to a pound of flour there will be 10 parts of fluorin per million parts of bread, which is 10 times the amount which was considered by Woodman to constitute an added constituent of beer.

Another poisonous impurity found, in four instances, in calcium acid phosphate, is arsenic, which was present to the extent of 16, 85, 100, and 200 parts, respectively, of arsenic trioxid per million parts of sample.

Inert fillers found to be added to commercial calcium acid phosphate or produced in the process of manufacture include starch and calcium sulphate. Eight samples of acid calcium phosphate obtained from the manufacturers or dealers contained 34.50, 35.60, 19.82, 5.43, 6.24, 0.57, 10.62, 17.64 per cent of starch, respectively; in two others starch was undetermined, but was present in determinable amounts. Three of these nine samples contained calcium oxid and sulphur trioxid in combining amounts calculating 41.84, 37.97, 8.77 per cent of calcium sulphate, alum being absent. The use of another filler has recently been observed, namely, a magnesium carbonate, which is apparently added for bulk.

It seems to the referee that the association can advantageously devote some attention to this matter of inert fillers, as well as to the question of the presence of determinable amounts of poisonous impurities in baking powder ingredients. It is recommended that further data be obtained along these lines.

REPORT ON FATS AND OILS.

By T. J. Bryan, *Associate Referee.*

Collaborative Work on the Detection of Fish Oil.

The work undertaken this year has been a continuation of that begun last year on the method of Eisenschiml and Copthorne for the detection of fish oil in the presence of vegetable oils. The method has been changed only as regards the temperature at which the bromination is conducted (namely, from 60° C. to 20° C.) and as regards the amount of oil taken for the test (from 3 to 6 grams). Last year the reports of collaborators showed the results of 70 tests, of which 15 led to false conclusions, 2 to doubtful ones, and 53 to correct ones. This year 75 tests gave 75 correct conclusions.

description of samples and directions for work.

Ten samples were sent to each collaborator, the description of which is given in the following list.

1. Cottonseed oil and 5 per cent bleached winter menhaden oil.
2. Cottonseed oil and 10 per cent bleached winter menhaden oil.
3. Peanut oil and 5 per cent Norwegian cod-liver oil.
4. Peanut oil and 5 per cent light pressed menhaden oil.
5. Cottonseed oil.
6. Linseed oil.
7. Olive oil and 5 per cent cod-liver oil, domestic.
8. Linseed oil and 5 per cent crude menhaden oil.
9. Linseed oil and 10 per cent crude menhaden oil.
10. Olive oil and 10 per cent cod-liver oil, domestic.

The directions sent to the collaborators were as follows:

You are requested to report on each sample for fish oil as present (P.) or absent (0). Please note in the method which follows the term "perfectly clear." If not "perfectly clear" report fish oil present.

Method.—Dissolve in a test tube about 6 grams of the oil in 12 cc of a mixture of equal parts of chloroform and glacial acetic acid. Add bromin drop by drop until a slight excess is indicated by the color, keeping the solution at about 20° C. Allow to stand fifteen minutes or more and then place the test tube in boiling water. If only vegetable oils are present, the solution will become perfectly clear, while fish oils will remain cloudy or contain a precipitate due to the presence of insoluble bromids.

Analytical Results.

The results obtained are given in the following table:

Qualitative tests for fish oil in the presence of vegetable oils.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.[1]	No. 6.[1]	No. 7.	No. 8.	No. 9.	No. 10.
H. S. Bailey	P.	P.	P.	P.	0	0	P.	P.	P.	P.
W. D. Richardson	P.	P.	P.	P.	(2)	0	P.	P.	P.	P.
E. M. Chace	P.	P.	P.	P.	0	0	P.	P.	P.	P.
A. Lowenstein	P.	P.	P.	P.	0	0	P.	P.	P.	P.
Paul Rudnick	P.	P.	P.	P.	0	0	P.	P.	P.	P.
R. W. Hilts	P.	P.	P.	P.	0	0	P.	P.	P.	P.
B. C. Gardner	P.	P.	P.	P.	0	0	P.	P.	P.	(2)
Byron McClelland	P.	P.	P.	(2)	(2)	(2)	P.	P.	P.	P.

[1] Cottonseed and linseed oils, respectively; all others contained fish oils, see page 87.
[2] Broken in transit.

COMMENTS BY COLLABORATORS.

R. W. Hilts: I observed that sample No. 6 gave a heavy precipitate of bromids in the cold, which, however, dissolved on heating. Samples Nos. 8 and 9 showed much more insoluble bromid in the cold than in the hot.

Paul Rudnick: The only comment that I have to make is that the quantity of fish oil present in Nos. 7 and 8 seemed to be very slight, as the solutions in these cases remained merely cloudy; in all the rest in which fish oil is reported as present, a more or less heavy precipitate remained upon heating.

E. M. Chace: The only doubtful sample is No. 6, which gave a heavy precipitate in the cold, but cleared up entirely after a few minutes boiling.

H. S. Bailey: In conjunction with this work I have applied the same test, as indicated in your method, to the following oils with the exception that the sample was measured (about 6.8 cc) instead of being weighed. The following results were obtained:

Whale oil: Heavy precipitate; after boiling turned nearly black.

Menhaden oil: Heavy bright orange precipitate.

Seal oil: Heavy light orange colored precipitate after heating.

Neatsfoot, Sesame, Corn, Olive, Cocoa Butter, Cocoanut, Chicken, Soy Bean, Poppy-seed, Palm, Linseed, Candlenut, Spindle, Oxidized Linseed, China Wood, and *Cottonseed* oils, none of which gave a reaction which would indicate the presence of fish oil with the exception of corn oil which was not absolutely clear even after heating.

It seems very probable from the results thus far obtained that the oil of marine animals, as well as fishes, gives an insoluble bromin compound.

B. C. Gardner: The method seems to me to be perfectly clear and to give definite results. On sample No. 9 the precipitate was very heavy and the test seemed to be a little more definite when a 3-gram sample was used.

Byron McClelland: Pure olive oil with this method gives a solution which is perfectly clear. Pure peanut oil with this method gives a solution which is perfectly clear. A mixture of olive oil and sardine oil gives a precipitate of insoluble bromids. A mixture of peanut oil and sardine oil gives a precipitate of insoluble bromids. A mixture of olive oil, peanut oil, and sardine oil gives a precipitate of insoluble bromids.

COMMENTS BY REFEREE.

Perfect results are very gratifying, but every precaution possible must be taken to make the interpretation of results a matter of certainty. That there has been uncertainty in the minds of some of those making the tests, is shown by the remarks in their reports with reference to the large amount of precipitate produced in the cold. That

the bromids of vegetable oils, unlike fish oils, are completely and perfectly dissolved in a boiling mixture of equal parts of chloroform and glacial acetic acid giving a perfectly clear solution, while the mixture is boiling hot, is the basis of this method. The amounts of bromids not soluble in the cold mixture is a matter of absolutely no import. There is only one condition under which the observations in the cold give any indications whatever as to the presence or absence of fish oil; that is in a case where the solution is absolutely clear in the cold (a condition not yet found) which would indicate the absence of fish oil. Fish oil has not been reported present in a single case when it was absent, and we feel that there will be no errors in reporting it absent when present, if one keeps in mind the complete solution and perfect clearness obtained in the boiling hot solution when fish oil is absent and that the slightest turbidity indicates the presence of fish oil.

No work has as yet been done with reference to the chemical composition of the bromids of fish oil insoluble in the boiling mixture. The method given is not applicable in the presence of metallic salts such as are used as driers in "boiled linseed oil." These metals must first be removed. The referee believes that the method should be adopted as a provisional method and has so recommended.

Preliminary Work on the Detection of Palm Oil.

SUGGESTED METHOD.

Acting under the instructions of the referee, B. C. Gardner, of the Illinois State food commission laboratory, has done some preliminary work with reference to securing a reliable method for the detecting of palm oil.

The modification of the Lieberman-Storch test for resin oil, proposed by Crampton and Simons,[1] was first investigated. In brief, the test consists in shaking 10 cc of the melted and filtered fat with an equal volume of acetic anhydrid, adding 1 drop of sulphuric acid (sp. gr. 1.53)[2] and again shaking the mixture for a few seconds. If palm oil be present the lower layers, on settling out, will be found to be colored blue with a tint of green.

DATA OBTAINED.

The following oils were examined, using the test just described. In all of these cases the color produced was very transitory, and on standing took on a greenish tinge.

Results on the detection of palm oil in various vegetable oils using the proposed method.

Kind of oil.	Color produced by oil.	Color produced by oil and 1 per cent of palm oil.
Cottonseed oil	Slight tint of green	Light blue color with green tint. Fades on standing.
Peanut oil	No color	Light greenish-blue. Fades on standing.
Sesame oil	Pink color, Darkens and turns greenish.	Pink tint. Darkens.
Mustardseed oil (filtered)	Light blue, green tint[3]	Light blue-green tint.[3]
Mustardseed oil (unfiltered)	Greenish-blue[3]	Greenish-blue.[3]
Oleo oil	Greenish-yellow	Light olive green.
Neutral lard	Light green	Light bluish-green.
Butter fat	Olive-green	Do.
Oleomargarin, No. 1[4]	do	Bluish-green, changes to olive green.
Oleomargarin, No. 2[5]	Light green	Do.

[1] J. Amer. Chem. Soc., 1905, 27: 270.
[2] 34.7 cc of sulphuric acid (1.84) and 35.7 cc of water.
[3] Gave same color.
[4] Oleomargarin No. 1 was composed of 55 per cent of oleo oil, 15 per cent of neutral lard, 10 per cent of peanut oil, and 20 per cent of June butter.
[5] Oleomargarin No. 2 contained 65 per cent of oleo oil, 25 per cent of neutral lard, and 20 per cent of cottonseed oil.

The oils were also tested, varying the amount of sulphuric acid used from one to four drops, the other reagents being the same. For cottonseed the results were as follows:

Detection of palm oil in cottonseed oil by the proposed method.

Drops of sulphuric acid.	Cottonseed oil.	Cottonseed oil and 1 per cent of palm oil.
1	Slight tint of green	Light blue color with tint of green.
2	Green with blue tint	Darker bluish-green.
3	Olive-green	Bluish-green.
4	Dark green	Dark green.

Practically the same results were obtained with the other oils, the color being developed when the amount of acid was increased, even though *no palm oil was present.*

CONCLUSION.

The test as described is not satisfactory for the following reasons:

(*a*) Other oils than palm oil give colors which are easily mistaken for the palm oil test.

(*b*) The color produced is not permanent. It changes shades and fades so rapidly that it is very difficult to recognize it.

(*c*) The test is not definite, as there is little difference in the color produced when palm oil is present and when it is absent.

(*d*) The color produced is changed so much by slightly varying the amount or strength of the sulphuric acid used.

A modification of this test, using glacial acetic acid in place of acetic anhydrid was tried with the idea of retarding the reaction and making the color more permanent. The results were very promising. The only interfering oils found were mustardseed oil and some samples of butter fat. Even these oils gave colors lighter in shade than did 1 per cent of palm oil. However, it was found that after repeatedly washing these oils with alcohol (8 or 10 times) and then drying on the steam bath to remove the last traces of alcohol, they no longer responded to the test. Oleomargarin No. 2, containing 1 per cent of palm oil was washed in the same manner 15 times and still gave a very good blue color when tested. The results obtained using glacial acetic acid were as follows:

Detection of palm oil in vegetable oils by the modified method.

Sample.	Color produced by oil.	Color produced by oil and 1 per cent of palm oil.
Cottonseed oil	No color	Definite blue color.
Peanut oil	do	Do.
Sesame oil	Yellowish color	Do.
Mustardseed oil (filtered)	Bluish-green [1]	Bluish-green.
Mustardseed oil (unfiltered)	Bright green [1]	Olive-green.
Oleo oil	No color	Definite blue color.
Neutral lard	do	Do.
Butter fat	Blue color [1]	Do.
Oleomargarin, No. 1	Tint of blue color [2]	Do.
Oleomargarin, No. 2	No color	Do.

[1] On washing with alcohol (as directed), these oils did not respond to test.
[2] Not enough color to call palm oil test.

Results on mixtures of oleomargarin, No. 2, and different percentages of mustardseed oil and palm oil, using the modified method.

Composition of mixture.			Color developed.
Per cent oleo, No. 2.	Per cent palm oil.	Per cent mustardseed oil.	
100	0	0	No color.
95	0	5	Do.
90	0	10	Do.
85	0	15	Light blue.[1]
80	0	20	Do.[1]
80	0	20	No color.[2]
94.5	.5	5.0	Light blue.
89	1.0	10.0	Dark blue.
0	0	100	Dark bluish-green.
0	0	100	No color.[2]

[1] Nearly same shade as produced by 0.5 per cent of palm oil.
[2] After washing with alcohol.

The oils were also tested using varying amounts of sulphuric acid (from one to four drops), but very little difference was noted, except in the case of the unwashed mustardseed oil, when the larger amount of acid deepened the color produced. In all these cases the color was permanent (from 10 to 60 minutes), and was a definite blue. Amounts of palm oil as low as 0.25 per cent were easily detected. This report is only preliminary, but seems to indicate that a colorimetric method could be worked out along this line.

ADDRESS OF PRESIDENT WITHERS: THE TEACHING OF CHEMISTRY IN AMERICAN AGRICULTURAL COLLEGES.

Introduction.

The collection of statistics is very difficult. One special difficulty in connection with the subject which I have selected is due to the number and kinds of courses in the American agricultural colleges. This paper will be confined to two phases of chemistry in the agricultural colleges, namely: First, the chemical instruction which is given to those who are preparing for agricultural work, and, second, the opportunities afforded in these institutions for preparing for careers in agricultural chemistry. With this purpose in mind, we must omit all consideration of the various engineering courses in these institutions, and also the various short agricultural courses, and the courses in the agricultural colleges for negroes, as the chemical work in both cases is generally below the college grade. The consideration of either of these classes of courses would of itself furnish sufficient material for a paper. These exclusions leave us the agricultural and the chemical courses. We shall first consider the four-year agricultural course. There are complications even here, on account of the large number of electives, which in effect give us several courses, such as in general agriculture, agronomy, horticulture, forestry, dairying, veterinary science, domestic economy, botany, etc. As not all of these can be discussed, data have been collected from one four-year course in each agricultural college, namely, the course in general agriculture or agronomy. The chemistry considered in these is the minimum requirement. In the second part of the paper there is discussed the maximum chemical instruction which it is possible for one to receive in these colleges.

Another difficulty is the great variety in the different institutions in expressing their requirements. In some cases there are given the requirements for the classroom and for the laboratory in the actual hours a week; in others the laboratory work is calculated to an equivalent of classroom work, and in other cases the classroom work is

calculated to an equivalent of laboratory work, and the two are expressed jointly. Even in this case there is no uniformity, as two hours, two and a half hours, and three hours, in different institutions are taken as the equivalent of one classroom hour. In some cases the actual number of hours is not given as for the week, but as the total actual hours for the third, the half, or the whole year. The unit system is followed in many institutions, and the unit is not uniform, referring in some cases to the third, in others to the half or the whole year, and varying in its representation from one to five hours a week. To make a comparison it is necessary to reduce these requirements to a single standard. The one selected is total classroom hours a week for the year, laboratory work being calculated to classroom work, and two hours of laboratory work being taken as the equivalent of one hour of classroom work.

The requirements for admission vary very much, and thus make a great difference in the grade of work. For example, in some cases mathematical study begins in the freshman year with algebra, in others with plane or solid geometry, in others with trigonometry, and in others all the mathematical study is required for entrance. Expressed by the Carnegie Foundation scale, the variation is from 2 or 3 points to about 14. The two uniform characteristics of the agricultural colleges are that there is at least one in each State and each has a 4-year course for graduation. The classification of States followed is that used by the Bureau of Education and other governmental departments.

General Chemistry.

In all the North Atlantic States (9) general chemistry begins in the freshman year, and in 1 State it continues 2 years. The number of hours a week given to the subject ranges from $2\frac{1}{2}$ to $5\frac{3}{4}$, the average being 4.

In the South Atlantic States (8) 4 begin the subject in the freshman year, 4 in the sophomore year, and in 1 the subject continues through the second year. The number of hours a week varies from 3 to $7\frac{1}{3}$, the average being 4.7.

In the North Central States (12) all but 2 begin the subject in the freshman year, and in 1 State it continues through the second year. The number of hours a week varies from 2 to $5\frac{1}{2}$, the average being 3.6.

In the South Central States (8) all but 2 begin the work in the sophomore year, and in 2 it continues through the second year. The number of hours a week varies from $1\frac{1}{2}$ to 6, the average being 4.6.

In the Far Western States (11), excepting 1, the information in regard to which is not available, 1 requires chemistry for admission, in 7 the subject is begun in the freshman year, and in 2 in the sophomore year. In 1 it is continued the second year. The number of hours a week varies from $2\frac{1}{2}$ to 8, the average being 4.2.

By groups the hours a week vary from 3.6 in the North Central States to 4.7 in the South Atlantic States, the average for the United States being 4.2. In 1 State general chemistry is required for admission, in 32 the study of it begins during the freshman year, and in 14 during the sophomore year, and in 6 it continues through the second year. Without a single exception laboratory work accompanies classroom instruction.

Organic Chemistry.

Organic chemistry is the branch of the subject which seems to be the least appreciated by those who have fixed the requirements of the course. Of the North Atlantic States 3 require the subject, in the South Atlantic States 5, in the North Central States 4, in the South Central States 3, and in the Far Western 3, making a total of 18, or only a little more than a third of the States. The number of hours a week varies from $1\frac{1}{3}$ to 5, the average being 1. It is quite likely that in addition to this a little time is given to the subject in connection with the introductory courses.

Agricultural chemistry, the first of the agricultural sciences, in point of time, may be said to date from 1840, if any definite date can be assigned. The work which

brought it into existence was prepared at the request of the chemical section of the British Association for the Advancement of Science. In the 1852 revision of Liebig's work by Lyon Playfair, the editor says, "The former edition of this work was prepared in the form of a report on the present state of organic chemistry." The title was "Organic chemistry in its application to vegetable physiology and agriculture." When the second part of his report, that relating to animal physiology and pathology, appeared in 1852, Liebig said, "The connection between chemistry and physiology is the same (i. e., "so fused." W. A. W.), and in another half century it will be found impossible to separate them." How could he know that about 1902 our knowledge of the carbohydrates and proteids and their cleavage products would have advanced so much? Will the agricultural colleges, while so highly honoring the memory of Liebig, at the same time minimize the subject, the knowledge of which made Liebig's work possible? Shall we say there is no connection between the altar and the gift upon the altar?

Analytical Chemistry.

Qualitative analysis is required in all of the North Atlantic States but 3, in all the South Atlantic States, in all the North Central States but 2, in all the South Central States but 2, and in all the Far Western States but 1, making a total of only 8 States in which it is not required. Quantitative analysis is required in 2 North Atlantic States, 4 South Atlantic States, 4 North Central States, 2 South Central States, and 4 Far Western States, making a total of 16 States in which quantitative analysis is required.

The average number of hours a week given to qualitative and quantitative analysis together is 1.5 for the North Atlantic States, 2.3 for the South Atlantic States and North Central States, 1.4 for the South Central States, and 2.7 for the Far Western States, with an average of 2 for the entire United States.

Agricultural Chemistry.

As taught to agricultural students, agricultural chemistry appears upon examination of the college catalogues to have three different meanings, namely, first, general chemistry, with such omissions and additions as will better fit the subject to the needs of agricultural students; second, quantitative analysis, with its scope similarly modified; and third, the consideration of plant and animal nutrition, the substances involved in these processes, and their products, useful and waste. The time spent along the lines mentioned under one and two is included in this paper under the heads of general chemistry and quantitative analysis, which have already been discussed. The time spent upon what is generally called agricultural chemistry averages 1.6 hours a week for a year in the North Atlantic States, 1.7 in the South Atlantic States, 1.6 in the North Central, 0.8 in the South Central, and 2 in the Far Western States, with an average of 1.5 for the whole United States. This average includes those institutions in which it is not required of agricultural students. The subject is not given at all, or is not required, in 5 North Atlantic States, in 1 South Atlantic State, in 4 North Central, 3 South Central, and 4 Far Western States, making a total of 17 States in which it is either not taught at all or not required. This is probably due to the fact that the matter which was formerly included under the term agricultural chemistry and taught by the chemistry department is now, in many cases, taught by other departments, under such names as soils, fertilizers, plant nutrition, animal feeding, etc. The lines representing the division of this work between the chemistry and the agronomy or animal husbandry departments, do not seem to be very clearly drawn. For example, we find that a certain well-known textbook is used in some institutions in the chemistry department for agricultural chemistry and in others by the agronomy department for soils. This condition of things will probably adjust itself in the best way.

A summary of these findings is included in the following table:

Branches of chemistry required in different colleges.

State group.	Inorganic.	Organic.	Analytical.	Agricultural.
North Atlantic	9	3	6	4
South Atlantic	8	5	8	7
North Central	12	4	10	8
South Central	8	3	6	4
Far Western	10	3	9	7
Total	47	18	39	30
States not requiring	0	29	8	17

Chemical requirements in agricultural courses expressed in hours a week for a year.

State group.	Inorganic.	Organic.	Analytical.	Agricultural.	Total.
North Atlantic	4.0	0.5	1.5	1.6	7.6
South Atlantic	4.7	1.7	2.3	1.7	10.2
North Central	3.6	.9	2.3	1.6	8.4
South Central	4.6	.6	1.4	.8	7.4
Far Western	4.2	1.0	2.7	2.0	9.9
Average	4.2	1.0	2.0	1.5	8.7

In 1897 the committee on methods of teaching agriculture reported to the Association of American Agricultural Colleges suggestions regarding a four-year course in agriculture. The matter relating to chemistry is as follows:

	Hours.
Chemistry (classroom work)	75
Chemistry (laboratory work)	75
Agricultural chemistry, in addition to general requirement	180

Taking, as we have done, two hours of laboratory work as the equivalent of one hour of classroom work, and 36 weeks as the length of the college year, the recommendations of the committee of the college association would amount to the equivalent of 8.1 hours a week for a year, while the figures compiled by us show that an average of 8.7 hours is actually given.

The estimate by the committee of agriculturists as to what should be done and the average of what is actually done agree very closely indeed, and the truth must be somewhere near these two figures. The close agreement is all the more remarkable when we consider the great variation in the different colleges. As time goes by probably the different colleges will conform more closely to these averages.

Undergraduate Work for Chemists.

The second portion of this paper relates to the opportunities offered by the agricultural colleges for training for chemical careers. Practically every agricultural college makes provision for such work (1) by offering electives in the agricultural or scientific courses; (2) by grouping these electives so that beginning with the junior or senior year of the agricultural course a student may devote a large part of his time to chemistry; and (3) by offering four-year courses in chemistry or chemical engineering. The different catalogues show an ample number of electives, but unless there are fully organized four-year courses it is impossible to tell how many students avail themselves of these opportunities, and further consideration of them must be omitted.

The report of the Bureau of Education shows the following students enrolled in chemical engineering and chemistry in the various agricultural colleges for the year 1908–9:

Report of Bureau of Education on chemistry students.

State.	Chemical engineering.	Chemistry.	State.	Chemical engineering.	Chemistry.
Maine	12	28	Missouri	16	.....
New Hampshire	19	.....	North Dakota	.....	4
Vermont	.....	33	North Central States	198	158
Rhode Island	7	.....			
New Jersey	.....	12	Kentucky	.....	25
Pennsylvania	11	65	Alabama	.....	22
			Louisiana	64	64
North Atlantic States	49	138	Texas	1	.....
			Arkansas	55	55
Maryland	.....	15	South Central States	120	166
Virginia	.....	34			
North Carolina	.....	17	Montana	.....	4
South Carolina	9	.....	Washington	.....	18
			California	51	.....
South Atlantic States	9	66	Far Western States.	51	22
Ohio	34	.....	Total for the United States	427	550
Indiana	51	19			
Illinois	59	48			
Wisconsin	23	41			
Minnesota	15	46			

Total students in chemical engineering and chemistry in the agricultural colleges, 977.

This list does not show fully the undergraduate work for training chemists, but for the reasons already stated the data for fuller information were not available.

Graduate Work in Chemistry.

Practically every agricultural college has a few graduate students doing work in chemistry for the master's degree. This is a secondary feature in some of the colleges, and others have well-digested schemes for work. A very valuable paper showing the scope and extent of graduate work in America appeared in Science this year, entitled "Doctorates Conferred by American Universities." From that paper we learn that 178 doctorates were conferred for work in science in 1910, about one-third of them by the universities of which the agricultural colleges are a part and about two-thirds by other institutions. Of this number, 44 were in chemistry, and about the same relation existed between the two classes of institutions. The 15 doctorates for work in chemistry were conferred by Cornell, Illinois, and Wisconsin. A table made from the paper referred to is inserted here, which shows, among other things, the very rapid development in the graduate departments of the universities of which the agricultural colleges are a part.

Doctorates conferred in the sciences.[1]

University.	Average for 10 years, 1898–1907.	1908.	1909.	1910.	Total for 13 years, 1898–1910.	In chemistry, 1910.
Cornell	10.4	15	24	27	170	4
Wisconsin	2.8	6	4	13	51	5
California	2.4	2	6	4	36	.....
Nebraska	1.3	1	2	1	17	.....
Illinois	.3	0	2	9	14	6
Minnesota	.7	1	2	1	11	.....
Missouri	.3	2	0	2	7	.....
	18.2	27	40	57	306	15
Other universities	105.1	157	152	121	1,481	29
Total in America	123.3	184	192	178	1,787	44

[1] Compiled from Science, August 19, 1910.

Agricultural Chemistry Teachers.

Bulletin No. 224 of the Office of Experiment Stations gives the organization of the different agricultural colleges in December, 1909. This publication shows that there are 228 teachers of chemistry in these institutions who come in contact with the students in agriculture. This list does not include all the chemistry teachers therefore. These are distributed approximately equally in the different sections, except that the South Atlantic Group has about half of her proportion, the deficiency being made up by the North Central Group. Of the 228, 51, or about one-fourth, have published enough research work to find a place in the Directory of American Men of Science, 1906 edition. This publication contains brief biographical sketches of those who by research work have contributed somewhat to the enlargement of our knowledge of the sciences. The figure given is an average of a little more than one for each college. In the number of teaching agricultural chemists named in the directory, the North Atlantic and North Central Groups lead, being about equal in number, and together they make up approximately three-fifths of the total number. The other groups are about equal, and each has approximately half as many as each of the two groups first named. The larger proportion of names comes from the chemists in the South Atlantic Division, which has 9 names in the directory out of a total of 24 chemists.

In the 1910–11 edition of Who's Who in America, 31 find a place, or about 1 out of every 7 of the 228. This publication contains the names of those who, on account of their achievements in some direction, have become subjects of more or less national interest. The greater number of agricultural college chemists, as in the case of the directory, comes from the North Central Division, which is followed closely by the North Atlantic Division. Together these make up three-fourths of the names, the other groups of States falling very far behind.

There is still another standard. The editor of the directory has prefixed a star to the names of about a thousand of those scientists whose work is supposed to be the most important. Of the 228 chemistry teachers in the agricultural colleges whose names appear in the organization list prepared by the Office of Experiment Stations, 9 appear in the directory with a star. Five of these are in the North Atlantic and four in the North Central Groups. There are no starred names in the South Atlantic, South Central, and Far Western Groups. These figures are shown in detail in the following table:

Classification of distinguished chemists teaching agricultural students in agricultural colleges.[1]

Groups of States.	Bul. 224, O. E. S.	American Men of Science.	Who's Who in America.	Starred names in American Men of Science.
North Atlantic States	49	14	10	5
South Atlantic States	24	9	2	.....
North Central States	73	15	13	4
South Central States	41	7	4	.....
Far Western States	41	6	2	.....
Total in United States	228	51	31	9

It may be interesting to determine how the chemist in the agricultural college compares with his fellow chemist when judged by the same standard. Information is lacking as to the exact number of chemists in America. There are 4,653 resident members of the American Chemical Society, and since many are not members of that society we know that there are more chemists than that in America. If from this number we subtract 228, the number of agricultural chemists, we shall have left 4,425. The nonagricultural college chemists furnish 168 starred names, or 1 name out of more than 31, while the agricultural college chemists furnish 1 starred name out of 25. This relative standing would be considerably increased were we to make correction for the number of chemists who are not members of the American Chemical Society. While it is doubtless a matter of pride that the agricultural chemist is assigned such high rank among American chemists by those who are considered by the editor of American Men of Science as the most capable judges, this fact should serve as a stimulus to greater effort to advance the cause of science, which we love, and of humanity, whose servants we are.

A special order for the election of officers was called for 10 o'clock Saturday morning, and the association adjourned to meet at 1.30 p. m.

FRIDAY—AFTERNOON SESSION.

REPORT OF COMMITTEE ON AMENDMENTS TO THE CONSTITUTION.

Chairman Van Slyke, on behalf of the committee, reported favorably on the adoption of the amendments to sections 1 and 2 of the constitution, proposed at the meeting of 1909, and the same were

[1] NOTE BY W. A. W.: Since the reading of this address the second edition of American Men of Science has appeared. It shows that the agricultural college chemists have made a net gain of 38 names in the directory and of 5 starred names. They have, therefore, not only maintained the relative rank previously assigned them, but have improved it. The distribution is shown by the following table:

Geographical distribution.	American Men of Science.	
	Total, 1910.	Starred, 1910.
North Atlantic States	19	6
South Atlantic States	12	.....
North Central States	28	8
South Central States	13	.....
Far Western States	16	.....
Total	88	14

adopted by the association. (These amendments are stated in Bulletin 132, pp. 168 and 169, and Circular 52, pp. 19 and 20. The constitution as amended will be found on p. 201 of this report.)

REPORT ON COCOA.

By W. L. Dubois, *Associate Referee.*

The collaborative work on cocoa and cocoa products was confined to the methods for the determination of sucrose and lactose in milk chocolate and to a short method for the determination of fat. Samples were sent to about ten collaborators and results received from those whose names appear in the table.

Sucrose and Lactose.

The method tried by the association, last year, for the determination of these sugars was originated by the present referee. This method depended upon the fact that lactose showed a dextro polarization at 87° C. and the determination of the sugar was made by heating the invert solution to this temperature and correcting the reading by various factors. Serious objections were offered to this manipulation, owing to the difficulty of obtaining satisfactory readings at such a high temperature, and in order to eliminate this source of inaccuracy, if possible, the following method was submitted to the collaborators for trial:

Transfer 26 grams of the finely divided material to an 8-ounce nursing bottle, add about 100 cc of petroleum ether and shake for five minutes.[1] The chocolate should be thoroughly disintegrated by this process. Whirl the bottle in a centrifuge until the petroleum ether is clear. Draw off the same by suction and repeat the treatment with petroleum ether. Place the bottle containing the defatted residue upon the top of a steam bath, or other warm place, until practically all of the residual petroleum ether is expelled. Add 100 cc of water and again shake until all of the chocolate is loosened from the sides and bottom of the bottle, and continue the shaking three minutes longer. Add 10 cc of basic lead acetate solution, mix thoroughly and filter through a folded filter. Make the direct polariscopic reading in a 200 mm tube on this solution, then precipitate from the same the excess of lead by means of dry potassium oxalate. Invert the filtrate by the method given at the top of page 41, Bulletin 107, Revised. It is unnecessary to neutralize the acid. Bring the invert solution to the temperature at which the direct reading was taken and make the invert reading. From the figures obtained calculate the approximate percentage of sucrose according to the following formula:

$$S=\frac{(A-B)\times 110}{142.66-\frac{T}{2}}$$

and the approximate percentage of lactose by the following formula:

$$L=\frac{(A\times 1.10)-S}{0.79^{2}}$$

In these formulas A equals the direct reading for normal weight, B, the invert reading for normal weight, S, the approximate percentage of sucrose, and L, the approximate percentage of lactose.

From the combined approximate percentages of sucrose and lactose found as above, calculate the approximate number of grams of sugar present in the 26 grams of sample taken. From the table given on page 256, Bulletin 107, Revised, determine the factor X to be applied to correct for expansion of solution due to dissolving the sucrose. True percentage of sucrose equals SX; true percentage of lactose equals LX.

Results obtained upon the sample of milk chocolate submitted for comparative work are given in the table.

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[1] We find, in the Buffalo laboratory, that this operation is best accomplished in a mechanical shaker of some sort.

[2] Specific rotation of lactose is 52.53; of sucrose, 66.37; the former divided by the latter gives 0.79.

Determination of sucrose and lactose in milk chocolate.

Analyst.	First determination.		Second determination.	
	Sucrose.	Lactose.	Sucrose.	Lactose.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
C. I. Lott, Buffalo, N. Y.	48.39	7.81	48.25	7.28
W. L. Dubois, Buffalo, N. Y.	47.53	7.56	.....	.....
R. W. Hilts, Philadelphia, Pa.	48.14	7.88	48.12	7.90
T. F. Pappe, Galveston, Tex.	48.15	7.68	.....	.....
E. H. Berry, Chicago, Ill.	47.45	9.30	.....	.....
N. Hendrickson, Omaha, Nebr.	48.05	7.79	.....	.....
E. R. Lyman, Portland, Oreg.	48.43	7.54	.....	.....
G. M. Bartlett, Boston, Mass.	48.33	8.62	48.17	8.70
B. B. Wright, New York, N. Y.	48.35	7.91	47.91	8.32

From these results it appears that this procedure is much superior to that of polarizing at 87° C.

COMMENTS BY ANALYSTS.

R. W. Hilts: I would like to suggest that instead of using the table on page 256 of Bulletin 107, Revised, to determine the increase in volume of the solution, due to the amount of sugar dissolved, the following simple formula could be used with convenience:

Volume=100+(G×0.62), when G=total sugar in grams and 0.62=volume in cubic centimeters displaced by 1 gram of cane sugar in water solution. I obtained the figure 0.62 by actual experiment on concentrations of from 2.5 to 15 grams of cane sugar in 100 cc, and found the displacement to run uniformly. Comparison of results by this formula with your original table shows that this formula gives results practically identical with the table mentioned. In using the table interpolation is almost always necessary, hence I think the use of this simple formula would, on the whole, be more convenient and just as accurate.

For the purpose of checking results by the polariscopic method as outlined for this year's work, I have also determined the sucrose (this doubtless should read "sugars") in this sample by copper reduction methods, with the following results: Lactose, 7.57, 7.52, and sucrose, 48.09 per cent.

I consider the determination of lactose by copper valuable as a check on the polariscopic method, particularly when only small amounts of lactose are present in the sample. Sucrose I think is best determined by the polariscopic method, and the above determinations by copper were simply made as checks. As a further comparison of these methods I include data obtained on a market sample of milk chocolate:

Comparison of polariscopic and copper reduction methods.

Method.	Lactose.	Sucrose.
	Per cent.	*Per cent.*
Polariscope	6.35	39.31
Copper	6.33	38.91

Will you pardon me for pointing out a slight inaccuracy in the method of calculation submitted in this year's work? A concrete example will best illustrate this. Assuming that there are 14.3 grams of combined sugars present in the 26 grams taken, this will displace 14.3×0.62=8.8 cc of water. If 100 cc of water and 10 cc of lead solution were added and the approximate sucrose content were calculated by formula—

$$S=\frac{(A-B)\times 110}{142.66-\frac{T}{2}},$$

it is incorrect to calculate the true sucrose content by formula S(approx.)×1.088. It is correctly given by S (approx.)$\times\frac{118.8}{110}$, or else by—

$$S=\frac{(A-B)\times 118.8}{142.66-\frac{T}{2}},$$

which is equivalent to the same thing. In the same manner the true lactose content is given by L (approx.)$\times\frac{118.8}{110}$.

Accordingly the true correction factor for volume occupied by dissolved sugar, under these conditions, is—

$$\text{Factor}=\frac{110+(G\times 0.62)}{110},$$

where G=approximate number of grams of total sugars.

Of course, if only (90+10) cc of water are added the factor is calculated by—

$$\text{Factor}=1.00+(G\times 0.0062).$$

In my opinion the polariscopic method for lactose and sucrose has been very much improved in this year's directions for collaborative work, particularly in that large factors are not involved in the calculation of lactose results, and because polarization at 87° C. is unnecessary.

T. F. Pappe: I have no criticism to make upon the method, except that it takes no account of any inversion of the cane sugar which might take place in the course of manufacture. This same criticism of course applies to the various reduction methods.

A. L. Winton: As to your formulæ for calculating "S" and "L," I can not help considering them ambiguous, for in them you say that "A" and "B" are direct and invert readings for normal weight, which carries with it correction for the dilution with the 10 cc of basic lead acetate, or at least may easily be so understood. Evidently that is not the intention as the factors 110 and 1.10 are intended to take care of this.

S. H. Ross: The determinations were made in duplicate with identical results. After adding 10 cc of basic lead acetate solution and mixing thoroughly, the bottles were whirled in centrifuge to facilitate subsequent filtration. Inversion was effected by the slow method, allowing to stand overnight.

E. R. Lyman: The method presented no difficulties and the polarization results on duplicate samples, run at the same time, were identical.

Polarization Results on Milk Chocolates.

In the analysis of milk chocolate, Bigelow and Albrech omit the preliminary extraction of fat with petroleum ether and use hot water instead of cold for dissolving the sugars, it being claimed that this procedure is more simple and rapid than that laid down above. In order to test this point the referee requested collaborators to do the following work:

(a) Transfer 26 grams of the finely divided material to an 8-ounce nursing bottle, add thereto about 100 cc of petroleum ether and shake for five minutes. Whirl the bottle in a centrifuge until the petroleum ether is clear, draw off the same by suction and repeat the treatment with petroleum ether. Add 100 cc of water and again shake until all of the chocolate is loosened from the sides and bottom of the bottle and continue the shaking three minutes longer. Add 10 cc of basic lead acetate solution, mix thoroughly and filter through a folded filter. Make the direct polariscopic reading in a 200 mm tube on this solution, reporting the same without making any corrections.

(b) Transfer 26 grams of the finely divided material to an 8-ounce nursing bottle, add 90 cc of water at room temperature, cork the bottle and place in a steam bath for 20 minutes, removing the stopper for a moment at the end of about 5 minutes for the purpose of releasing the pressure. Twice during the 20-minute period shake the bottle thoroughly so as to completely emulsify the chocolate solution. Remove the bottle from the steam bath and cool to room temperature, add 10 cc of basic lead acetate solution, mix thoroughly and filter through a folded filter. Make the direct reading on this solution in a 200 mm tube, reporting the same without correction.

Polarizations obtained by the collaborators and calculated to the same concentration of solution appear in the following table:

Cooperative polarizations on milk chocolate by two methods.

Analyst.	Polarization.		Analyst.	Polarization.	
	Method (a).	Method (b).		Method (a).	Method (b).
Wright, B. B., New York, N. Y.	49.72	49.80	Hendrickson, N., Omaha, Nebr.	50.49	50.00
	.....	50.00			
	.....	49.50	Lyman, E. R., Portland, Oreg.	49.61	49.60
Berry, E. H., Chicago, Ill.	49.83	49.50			
Hilts, R. W., Philadelphia, Pa.	53.99	53.91	McClelland, B., New York, N. Y.	50.27	50.10
				50.38	50.00
Smith, F. G., St. Paul, Minn.	50.93	50.00			

The following opinions and criticisms of the point in question were submitted by the different analysts:

COMMENTS OF ANALYSTS.

B. G. McClelland: There is very little choice between the two methods, that involving extraction of fat by petroleum ether requiring a little more time and manipulation, but the latter is of a more pleasant character. Method (b) requires less manipulation, but necessitates work with bottles at a high temperature, and there is more or less danger of being scalded. With these exceptions there seems to be very little choice between the two methods.

E. R. Lyman: As no difficulties were met at any stage in either method, I am decidedly of the opinion that method (b) is more expeditious, especially when no mechanical shaker is at hand. Moreover, method (a) requires a considerable quantity of petroleum ether, which in our laboratory we have to prepare by redistilling 86° gasoline. If the latter will answer the purpose this objection does not apply. The filtrate in method (b) was a little slower, due, no doubt, to the greater concentration.

S. H. Ross: Method (b) appears to have some advantage over method (a) in that less time was actually consumed in the manipulation, and the determination was completed in a shorter space of time.

A. S. Mitchell: It will be noted that after correction for volumes of water and lead acetate solutions added, (a) appears to give the more perfect extraction.

R. W. Hilts: The omission of the fat extraction seems to be an excellent suggestion, as it offers no difficulties and saves time, but I think it should be tested more thoroughly. The use of a 200 cc erlenmeyer might be more convenient, as there is less danger of breakage than with a thick-glass nursing bottle. There is, of course, a question as to whether the hot water may not dissolve some of the starch. I found, however, that the lead-free filtrates gave only a very faint test with iodin. In the presence of a foreign starch the method might not be applicable.

B. B. Wright: I found method (b) very satisfactory as to manipulation. I had considerable trouble with corks blowing out when bottles were in the steam bath the first few minutes. Nos. 2 and 3 I did not stopper until the bottles had been in the steam bath about three minutes and the air had ceased to expand. I found that method (b) required less time than (a), and I consider it the simpler method.

W. L. Dubois: Satisfactory for milk chocolate. For cocoa, however, filtration was very slow and the filtrate cloudy.

MODIFIED STATEMENT OF METHOD.

It seems to the referee that several of these criticisms and suggestions can be applied to the method to its advantage. The following modified statement is, therefore, presented to the association:

Prepare the sample by chilling well and shaving it with a knife as finely as possible. Transfer 26 grams of this material to an 8-ounce nursing bottle, add thereto about 100 cc of petroleum ether and shake for five minutes; this operation being greatly facili-

tated by the use of a mechanical shaker. The chocolate should be thoroughly disintegrated by this process. Whirl the bottle in a centrifuge until the petroleum ether is clear. Draw off the same by suction, and repeat the treatment with petroleum ether. Place the bottle containing the defatted residue on the top of a steam bath, or other warm place, until practically all of the residual petroleum ether is expelled. Add 100 cc of water and again shake until all of the chocolate is loosened from the sides and bottom of the bottle and continue the shaking three minutes longer. Add basic lead acetate solution from a burette until no more precipitation takes place, and then add sufficient water to make the total volume of liquid 110 cc, mix thoroughly, and filter through a folded filter. Make the direct polariscopic reading (A) in a 200 mm tube on this solution, then precipitate from the same the excess of lead by means of dry potassium oxalate. Invert the filtrate by one of the methods given on page 41, Bulletin 107, Revised. It is unnecessary to neutralize the acid. Bring the invert solution to the temperature at which the direct reading was taken and make the invert reading, multiplying the same by 2 to correct for dilution (B). From the figures obtained calculate the approximate percentage of sucrose (S) according to the following formula:

$$S=\frac{(A-B)\times 110}{142.66-\frac{T}{2}},$$

and the approximate percentage of lactose (L) after the formula—

$$L=\frac{(A\times 1.10)-S}{0.79}.$$

From the combined approximate percentages of sucrose and lactose found as above calculate the approximate number of grams of sugar present in the 26 grams of sample used. Determine the factor X by the following formula:

$$X=110+(G\times 0.62),$$

in which G = the approximate amount of sugar present, found as above, and 0.62 = the volume in cc displaced by 1 gram of sugar in water solution. Applying this correction:

$$\text{True per cent of sucrose}=\frac{SX}{110},$$

$$\text{True per cent of lactose}=\frac{LX}{110}.$$

A table is appended giving results obtained by the referee on a number of commercial milk chocolates other than those submitted to the collaborators:

Sucrose and lactose results on commercial milk chocolates by the referee.

Sample.	Sucrose.	Lactose.	Sample.	Sucrose.	Lactose.
	Per cent.	*Per cent.*	Commercial—Continued.	*Per cent.*	*Per cent.*
Laboratory[1]	36.4	8.8	4	54.3	3.3
	36.6	8.6		54.5	3.1
Commercial:			5	41.1	7.2
1	49.2	8.3		41.3	7.2
	49.0	8.5	6	47.6	7.9
2	43.7	7.3		47.5	7.9
	43.9	7.3	7	44.9	3.3
3	41.5	8.5	8	50.3	4.5
	41.5	8.7		50.5	4.3

[1] The sample prepared in the laboratory contained 36 per cent sucrose and 9 per cent lactose.

Determination of Fat.

It is often desired in the course of the analysis of cocoa products to make a quick determination of the fat content. The present official method involving extraction for 16 hours, the grinding of a partially extracted sample after the expiration of a certain part of this time, and the weighing and cleaning of the flasks involves much labor, so that a method which is more rapid would have many advantages even

though applicable only to samples on which approximate results were desired. The referee adopted for trial by the association a method devised by Bigelow and Albrech and used with success in the Bureau of Chemistry.

METHOD AND ANALYTICAL RESULTS.

Transfer 2 grams of finely ground sample to a narrow mouth, 4-ounce bottle, add 50 cc of anhydrous ether from a burette or pipette, and stopper the bottle immediately with a sound cork. Shake about 10 minutes and whirl in a centrifuge until the cocoa material is securely packed in the bottle. Fill a burette to the lower mark (50 cc mark) with ordinary ether, place a small funnel and filter paper in the top, and pour the supernatant solution from the bottle through the filter into the burette, care being taken to pour the solution in such a way as to disturb the cocoa material as little as possible. Ether having been previously run into the burette to the lower mark it is now a simple matter to read off the amount of fat solution recovered from the bottle. This will vary in different cases from 45 to 48 cc. (The use of the burette for measuring the fat solution in this way is necessary, owing to the apparent absorption of a few cubic centimeters of ether by the cocoa material.) Run the ether from the burette into a small, tared Erlenmeyer flask of about 4-ounce capacity, washing the burette several times with ordinary ether and adding the washings to the flask. Evaporate the ether and weigh as usual in fat determinations. The fat is calculated from the weight of the residue by the following formula:

$$\text{Percentage of fat} = \frac{25X}{Y} \times 100,$$

in which X = the weight of the residue or fat in the flask after evaporation, and Y the number of cubic centimeters of ether recovered.

One sample each of cocoa, chocolate, and milk chocolate was submitted for comparative analysis with the results in the table:

Cooperative results on determination of fat in cocoa, chocolate, and milk chocolate.

Analyst.	Short method.			Official method (16 hours).		
	A (cocoa).	B (chocolate).	C (milk chocolate).	A (cocoa).	B (chocolate).	C (milk chocolate).
C. I. Lott, Buffalo, N. Y.	25.37	54.25	29.57	.....	.....	.....
W. L. Dubois, Buffalo, N. Y.	25.18	53.94	29.56	25.35	54.89	29.70
E. R. Lyman, Portland, Oreg.	25.21	54.78	29.54	.....	.....	.....
	25.40	54.82	29.54	.....	.....	.....
E. H. Berry, Chicago, Ill.	26.40	55.50	29.97	.....	.....	.....
	26.17	57.08	30.19	.....	.....	.....
T. F. Pappe, Galveston, Tex.	24.92	54.42	29.17	24.95	54.56	29.32
	25.55	55.13	29.35	.....	.....	.....
N. Hendrickson, Omaha, Nebr.	25.17	54.93	29.55	.....	.....	.....
	25.39	54.29	29.97	.....	.....	.....
F. G. Smith, St. Paul, Minn.	24.9	54.0	30.0	.....	.....	.....
	Lost.	54.4	29.6	.....	.....	.....
B. B. Wright, New York, N. Y.	25.08	53.62	29.75	.....	.....	.....
	25.03	.....	29.90	.....	.....	.....
	25.44	54.30	.....	.....	.....	.....
	25.04	54.73	.....	.....	.....	.....
B. McClelland, New York, N. Y.	23.7	54.00	30.04	25.27	54.73	29.63
	23.23	54.50	30.02	25.21	54.69	29.43
	[1] 25.55	.....	.....	.....	.....	.....
M. C. Albrech, Pittsburg, Pa.	24.96	54.63	.....	.....	.....	.....
	24.95	54.60	.....	[1] 25.08	[2] 54.64	.....
	.....	.....	.....	.....	[2] 54.36	.....

[1] Run on warm day.

[2] Thirty-six hours.

COMMENTS BY ANALYSTS.

A. S. Mitchell: The method is simple and valuable for inspection in any event.

T. F. Pappe: In regard to this method, it seems to me to be of little value in this climate (Galveston, Tex.). It is almost impossible to measure and manipulate ether solutions quantitatively with a temperature running from 25° to 32° C. Aside from

this fact I do not think that the method is rapid enough to compensate for the inaccuracies. There is more manipulation, and the time required in actual work is much longer than by the official method.

E. R. Lyman: The method presented no difficulties, and the results on duplicates are surprisingly close. The first two samples were not centrifuged so long as the last and the fat residue showed the presence of a trace of cocoa powder. The fat from sample "C" showed no trace of cocoa powder.

C. S. Brinton: Sample "A" was examined on a very warm day and considerable evaporation of ether took place during the filtering. This of course has a tendency to give high results, and for this reason alone I think the method should be rejected. From experience in this laboratory (Philadelphia) I do not think that the proposed method is going to be satisfactory except in winter, at a time when the operation can be conducted in a cool room.

M. C. Albrech: I used an 8-ounce bottle instead of a 4-ounce bottle and did not filter the ether solution. I am of the opinion that filtering the ether solution would be likely to introduce an error. Sample "C" I did not run, for the reason that it was so hot here at the time that the fat was sticking all over the inside of the bottle, and I knew I could not get any comparative results. The other two samples were run on a day when the temperature was about 30° C. in the laboratory.

B. B. Wright: I found it required about 20 minutes to obtain a clear filtrate. I should think that the results might vary somewhat, depending upon room temperature. If the ether was near boiling point when filtered, some of the loss ascribed to the loss of ether by cocoa would really be evaporation and tend to raise the percentage of fat. Possibly this loss would be too small to consider.

COMMENTS BY REFEREE.

From these reports it would appear that this method is of considerable value when results are desired in a much shorter time than that required by the official method. In fact, the figures reported by the collaborators are practically as close to each other and to the results obtained on these three samples by the official method as one would expect to receive from this number of analysts working in different parts of the country and using the continuous-extraction method. It appears to the referee that in many cases the method in question might prove more accurate than that of long extraction with ether, regrinding, and additional treatment with the solvent, inasmuch as the extract obtained on the cocoa after removing the same from the thimble and grinding, preparatory to an additional extraction of some hours, appears to be frequently composed of material other than fat. In fact, from experiments under way, though not yet completed, it would seem that a duration of four or five hours in the official method would give as accurate results as that of 16 hours now employed. Results obtained from the former cases, if inaccurate, would probably be too low, whereas in the referee's opinion results obtained by extracting 16 hours or more are invariably too high. A table of results is appended giving the figures obtained on a number of samples of different kinds of cocoa products by both the official method and the short method under consideration, nine of the former samples being run for four hours, the ether extract calculated, and the sample extracted for an additional 12 hours. The amount obtained by this additional period of extraction will be seen to vary from 0.04 to 0.45 per cent.

Results on the determination of fat in commercial samples by the official method and by the proposed short method.

Sample.	Official method varying time of extraction.					Sample.	Official method varying time of extraction.				
	4 hours extraction.	Additional 12 hours extraction.	Total.	24 hours continuous extraction.	Short method.		4 hours extraction.	Additional 12 hours extraction.	Total.	24 hours continuous extraction.	Short method.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*		*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Cocoa	.....	.....	.....	24.50	24.64	Milk chocolate—Con.					
Do	.....	.....	.....	27.21	27.04	Do	31.04	0.28	31.32	.....	31.82
Do	.....	.....	.....	24.33	24.79	Do	30.37	.16	30.53	.....	30.23
Do	.....	.....	.....	22.96	22.99	Do	33.59	.36	33.95	.....	33.98
Chocolate	.....	.....	.....	52.74	51.77	Sweet chocolate					
Do	.....	.....	.....	51.44	50.93		24.24	.28	24.52	.....	24.11
Do	.....	.....	.....	53.74	52.72	Do	27.56	.04	27.60	.....	27.64
Do	.....	.....	.....	53.57	53.27	Do	19.32	.14	19.46	.....	19.52
Milk chocolate	30.25	0.45	30.70	.....	30.51	Do	29.18	.06	29.24	.....	29.07
						Do	25.40	.20	25.60	.....	25.32

Recommendations.

It is recommended—

(1) That the method for sucrose and lactose tried this year be adopted as provisional, being substituted for the one on page 256, Bulletin 107, Revised.

(2) That the optional method of dissolving the sugars by the use of hot water be further studied.

(3) That the method for determination of fat be further studied.

REPORT ON TEA AND COFFEE.

By M. E. Jaffa, *Associate Referee.*

It was decided to confine the work this year to the determination of caffein in coffee. No cooperative investigations were carried on because it was considered better to have the work done by two expert analysts and to base recommendation for later cooperative work on their results, rather than to attempt to obtain the first data from a large number of chemists of varied degrees of experience with this line of work.

Methods for Caffein Determination.

Provisional method (*A*).—As given in Bulletin 107, Revised, page 153.

Modification (*B*).—Moisten residue left in extraction thimble after the first 5-hour extraction with 5 cc of water, let stand one hour and extract with chloroform for five hours. Weigh impure caffein and determine nitrogen in residue by Kjeldahl method. (N×3.464=caffein.)

Modification (*C*).—Modification used in the New York Food and Drug Inspection Laboratory. Evaporate filtrate after precipitating the excess of lead, to a volume of about 50 cc, make slightly alkaline with sodium hydroxid, transfer to a separatory funnel and extract five times with chloroform, using 25 cc, 20 cc, 20 cc, 15 cc, and 10 cc, respectively. Transfer to Kjeldahl flask, distil off the chloroform and determine nitrogen in the residue by the Kjeldahl or Gunning method. Nitrogen multiplied by 3.464 equals caffein.

Modification (*D*).—To from 5 to 10 grams of coffee add 100 cc of water, boil, filter, and treat the residue twice more with boiling water. Add to united filtrates an excess of lead acetate, filter, and wash. Treat the filtrate with hydrogen sulphid to remove excess of lead, filter, wash, and evaporate filtrate to dryness in a Hoffmeister Schälchen with some sand and a little magnesia. Crush Schälchen between filter papers,

transfer to Soxhlet extraction apparatus, moisten residue with a small amount of hot water, (about 5 cc,) and allow to stand for one hour, thereby rendering the caffein readily soluble in the solvent. Extract with chloroform for 3 to 5 hours. Dry the chloroform residue at 100° C. and weigh as caffein, transfer residue to Kjeldahl flask with a small amount of hot water and determine nitrogen by Kjeldahl or Gunning method. Multiply nitrogen found by 3.464 to obtain the amount of caffein present.

Gorter method.—Moisten 11 grams of finely powdered coffee with 3 cc of water, allow to stand for half an hour, and extract for 3 hours in a Soxhlet extractor with chloroform. Evaporate the extract, treat residue of fat and caffein with hot water, filter through a cotton plug and moistened filter paper, and wash with hot water. Make up the filtrate and washings to 55 cc, pipette off 50 cc and extract four times with chloroform. This chloroform extract is evaporated in a tared flask and the caffein dried at 100° C. and weighed. Transfer residue to Kjeldahl flask with a small amount of hot water and determine nitrogen by Kjeldahl or Gunning method. Nitrogen multiplied by 3.464 equals caffein.

ANALYTICAL DATA.

Determination of caffein in different varieties of coffee, using different methods (Stewart and Mehrtens).

Method.	De-caffeinated.	Costa Rica.	Java.	Mocha.	Salvador.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Gorter method (N×3.464)	0.14	1.33	1.27	1.22	1.31
	.....	1.34	1.28	1.22	1.38
Provisional method (A) (5-hour extraction)	.417	1.531	1.461	1.369	1.296
Increase by moistening with water and reextracting for five hours (B)	.091	.126	.156	.188	.465
Total gravimetric, (A) plus (B)	.508	1.657	1.617	1.557	1.761
Total N×3.464, (A) plus (B)	.16	1.34	1.25	1.21	1.37
Provisional method (C) (N×3.464), extraction in separatory funnel	.14	1.30	1.21	1.19	1.31
Provisional method (D), gravimetric	.369	1.486	1.541	1.476	1.547
Provisional method (D), N×3.464	.14	1.33	1.25	1.22	1.32
Lendrich and Nottbohm (gravimetric)	.....	.....	1.14	.....	.....
	.....	.....	1.18	.....	.....

COMMENTS OF COLLABORATORS (A. R. MEHRTENS AND G. R. STEWART).

A consideration of the results of last year's work showed that the present provisional method did not yield all the caffein on the first chloroform extraction; a second chloroform extraction after moistening the residue was found to yield additional caffein.

The same difficulty has been experienced by other workers on Juckenack and Hilger's method,[1] a moist condition of the residue being necessary for complete extraction of the caffein. In taking up this year's work it was therefore decided to thus modify the present provisional method and also to continue the study of the Gorter method.

Method (A).—The chloroform used contained a slight trace of moisture. The extraction was continued for 5 hours.

Modification (B).—The residue from A was moistened in the extraction thimble with 5 cc of cold water and reextracted for five hours with chloroform. By this modification a slight increase of caffein was obtained from each sample. The nitrogen was then determined in the combined residues and it was found that an appreciable quantity of impurities had been extracted with the caffein. We are therefore inclined to believe that the gravimetric determination should not be taken as a final result.

Modification (C).—This consisted of the direct extraction in a separatory funnel of the clarified, lead-free filtrate, obtained as in (A), after concentration to a volume of 50 cc. The residue, being decidedly colored, was not weighed, but the nitrogen determined by the Kjeldahl method. The results obtained agreed closely with those found by other methods.

Modification (D).—The residue obtained from this modification was also contaminated by coloring matter, etc., therefore caffein was calculated from nitrogen in addition to direct weighing.

The Gorter method was carried out exactly as outlined in Bulletin 132, page 135, with the exception that it was found necessary to pass the solution through a moistened

[1] K. Lendrich and R. Murdfield, Zts. Nahr. Genussm., 1908, **16**: 647–658.

filter paper in addition to the cotton plug in order to obtain a perfectly clean filtrate. As a whole we believe that the results as obtained by this method were the most satisfactory of those studied with regard to ease and rapidity of manipulation; but like the provisional method, the residue was too highly colored to give an accurate gravimetric determination.

In addition to these a careful examination was made of the literature on the subject and the method of K. Lendrich and E. Nottbohm [1] was tried on one sample. While the results were slightly low, the caffein was clean and weighable. This method seems deserving of further investigation, and is stated in detail as follows:

THE LENDRICH-NOTTBOHM METHOD.

This method is the result of a considerable amount of research work, each operation involved in the process—namely, the preparation of the sample, the extraction, the treatment with permanganate, the separation of the oil, etc., and the final extraction of the caffein—having been submitted to an exhaustive examination in order to ascertain the procedure giving the most trustworthy result.

Twenty grams of the raw or roasted coffee, ground so as to pass through a sieve of 1 mm mesh, are moistened with 10 cc of water, and the mass is stirred from time to time for a period of two hours. The moist powder is then transferred to an extraction thimble and extracted with carbon tetrachlorid for three hours. To the extract thus obtained is added 1 gram of solid paraffin, the carbon tetrachlorid is evaporated, and the residue is extracted with four successive quantities of boiling water, using 50 cc of the first extraction, and then three quantities of 25 cc each. The united aqueous extracts are cooled, passed through a moistened filter, and the latter is washed with hot water. In order to remove coloring matters and other substances which are extracted together with the caffein, the filtrate is next treated at the ordinary temperature with from 10 to 30 cc—that is, a slight excess of 1 per cent potassium permanganate solution. At the end of 15 minutes the excess of permanganate is decomposed by the addition, drop by drop, of 3 per cent hydrogen peroxid solution containing 1 per cent of acetic acid. The whole is then heated for 15 minutes on a boiling water-bath and filtered, the residue, consisting mainly of manganese dioxid, being washed with boiling water. The filtrate and washings are evaporated to dryness, the residue is dried in the steam-oven for 15 minutes, and at once extracted with warm chloroform. The chloroform solution is then evaporated, and the residue of caffein obtained is weighed, after being dried at a temperature of 100° C. for 30 minutes. Instead of evaporating the filtrate obtained after the permanganate treatment, if preferred, it may be extracted directly with chloroform, and in cases where the greatest accuracy is desired the nitrogen may be estimated in the residue of caffein, and the alkaloid then calculated from the quantity of nitrogen found. It is shown, however, that the residue of caffein obtained in the above process is practically pure. With slight alterations the process may be applied to the estimation of caffein in coffee extracts (essences) and in drugs containing caffein; it is also applicable to the estimation of theobromin in drugs.

Other methods considered are as follows:

Beitter. Neuere Erfahrungen über Coffeïnbestimmungen. (*In* Chem. Ztg. 1901, **25** (81): 869.)

Brunner, H., and Leins, H. Über die Trennung und quantitative Bestimmung des Caffeïns und Theobromins. (*In* Schweiz. Wochens. Chem. Pharm. 1898, **36**: 301–303; Chem. Centrbl. 1898, **69** (2): 512.)

Delacour, A. Dosage de la caféine dans le thé, le café, etc. (*In* J. pharm. chim. 1896, 6th ser., pt. 4, pp. 490–491.)

Dieterich, K. Über die Wertbestimmung der Kolanuss und des Kolaextraktes. (*In* Pharm. Ztg. 1897, **42**: 647–650; Chem. Centralbl. 1897, **68** (2): 977.)

Forster, A., and Riechelmann, R. Zur Bestimmung des Caffeïns im Kaffee. (*In* Zts. öffentl. Chem. 1897, **3**: 129–131, 235–236; Chem. Centralbl. 1897, **68** (1): 1259; **68** (2): 436.)

Gadamer, J. Ueber Koffeinbestimmungen in Thee, Kaffee und Kola. (*In* Arch. Pharm. 1899, **237**: 58–68; Chem. Centralbl. 1899, **70** (1): 713.)

Gorter, K. Beiträge zur Kenntnis des Kaffees. (*In* Ann. Chem. (Liebig) 1908, **358**: 327–348.)

[1] Zts. Nahr. Genussm., 1909, **17**: 241–265; Analyst, 1909, **34**: 214.

Graf, L. Über den Zusammenhang von Coffeïngehalt und Qualität bei chinesischem Thee. (*In* Forschungs-Berichte über Lebensmittel und ihre Beziehungen zur Hygiene über forense Chemie und Pharmakognosie, 1897, **4**: 88–89; Chem. Centralbl. 1897, **68** (1): 1248–1249.)

Hilger, A., and Juckenack, A. Zur Bestimmung des Coffeïns im Kaffee und Thee. (*In* Forschungs-Berichte über Lebensmittel und ihre Beziehungen zur Hygiene über forense Chemie und Pharmakognosie, 1897, **4**: 49–50, 145–154; Chem. Centralbl. 1897, **68** (1): 775, **68** (2): 233.)

Katz, F. Ueber die quantitative Bestimmung des Kaffeins. (*In* Ber. d. pharm. Ges. 1902, **12**: 250.)

Keller, C. C. Die Bestimmung des Coffeïns im Thee. (*In* Ber. d. pharm. Ges. 1897, **7**: 105–112; Chem. Centralbl. 1897, **68** (1): 1134.)

LaWall, C. H. Detection of small quantities of caffeine. (*In* Amer. J. Pharm. 1909, **81**: 218.)

Lendrich, K., and Murdfield, R. Über eine erhebliche Fehlerquelle bei der Bestimmung des Coffeins nach dem Verfahren von Juckenack und Hilger. (*In* Zts. Nahr. Genussm. 1908, **16**: 647–658.)

Lendrich, K., and Nottbohm, E. Über den Coffeingehalt des Kaffees und den Coffeinverlust beim Rösten des Kaffees. (*In* Zts. Nahr. Genussm. 1909, **18**: 299–308.)

Lendrich, K., and Nottbohm, E. Verfahren zur Bestimmung des Coffeins im Kaffee. (*In* Zts. Nahr. Genussm. 1909, **17**: 241–265.)

Puckner, W. A. Notes on the determination of caffeine. (*In* Amer. J. Pharm. 1905, **77**: 488.)

Seidell, A. The solubility of acetanilide, phenacetine, caffeine, and salol in several solvents. (*In* J. Amer. Chem. Soc. 1907, **29**: 1088–1091.)

Tassilly, E. Sur un nouveau procédé de dosage de la caféine dans le café. (*In* Société chimique de France. Bulletin. 1897, 3d ser. **17**: 766–768.) Über ein neues Verfahren zur Bestimmung des Caffeïns im Kaffee. (*In* Chem. Centralbl. 1897, **68** (2): 644.)

Tattock, R. R., and Thompson, R. T. Analysis and composition of coffee, chicory, and coffee and chicory essences. (*In* J. Soc. Chem. Ind. 1910, **29**: 138–140.)

Trillich, H., and Göckel, H. Beiträge zur Kenntnis des Kaffees und der Kaffeesurrogate. (*In* Forschungs-Berichte über Lebensmittel und ihre Beziehungen zur Hygiene über forense Chemie und Pharmakognosie, 1897, **4**: 78–88; Chem. Centralbl. 1897, **68** (1): 1248.)

REPORT ON PRESERVATIVES.

By P. B. Dunbar, *Associate Referee.*

Quantitative Estimation of Sodium Benzoate.

At the last meeting of the Association, a method[1] was proposed for the determination of sodium benzoate in ketchup, based on that of LaWall and Bradshaw.[2] The results obtained with this method by the various collaborators were so encouraging that it was decided to continue work on it during the present year, applying it to the determination of sodium benzoate in other food products.

As was stated last year, chloroform is used as the solvent in this method because it extracts benzoic acid completely from saturated salt solution while it dissolves only traces of mineral acids and other interfering substances, making it unnecessary to wash the extract. Being heavier than water, it can be drawn off from the bottom of the separatory funnel, an obvious advantage; moreover, it is not inflammable.

To avoid loss of benzoic acid by volatilization, it is desirable to evaporate the chloroform extract spontaneously or in a current of dry air. Where a blast is not convenient this is sometimes a lengthy procedure. A number of experiments were, therefore, made to determine whether any considerable loss of benzoic acid occurs when the chloroform extract is distilled to a small volume at low temperature. One hundred and fifty cubic centimeter portions of a chloroform solution containing 0.7 gram of benzoic acid per liter, were evaporated under a blast of air which had been

[1] U. S. Dept. Agr., Bureau of Chemistry Bulletin 132, pages 143–144.
[2] Amer. J. Pharm., 1908, 80: 171.

passed over calcium chlorid. After evaporation of the chloroform the residue was dried overnight in a sulphuric-acid desiccator, then taken up in neutral alcohol, and titrated with twentieth-normal sodium hydroxid. Other 150 cc portions of the same solution were distilled on an electric hot plate so slowly that the chloroform came over drop by drop. When the volume of the solution was reduced to about 40 cc it was transferred to an evaporating dish and the flask rinsed with a little chloroform. The remaining chloroform was then evaporated in a current of dry air and the residue treated as in the preceding experiment. The results showed that where the chloroform was evaporated by means of a blast the percentages of recovery of benzoic acid were 98.76, 99.48, and 99.34. By the distillation method the recovery was 96.66, 96.61, 98.27, and 99.61 per cent. This indicates that when proper care is exercised in carrying on the distillation the loss by this method is trifling.

At the last meeting of the association two methods for the determination of sodium benzoate in jam, proposed by A. E. Taylor, were reported.[1] The few results which were reported were very satisfactory. These methods have been tested during the past year. They are as follows:

Method No. 1.—Make 150 grams of the sample alkaline with 50 cc of milk of lime and dilute to 500 cc with water. Allow the mixture to stand for two hours with frequent shaking and then filter through a large folded filter. Acidify 150 cc portions of the filtrate with sulphuric acid and extract with ether, using successive portions of 70, 50, 40, and 30 cc. In each extraction and in the combined extract make three washings with water, using 3 cc for each washing. Then evaporate the ether solution in a current of air, dry the residue over sulphuric acid overnight, and titrate in neutral alcohol solution in the usual manner.

Method No. 2.—Follow the same procedure as in the preceding method, except that instead of adding milk of lime make the material slightly alkaline with dilute sodium hydroxid, add 15 to 20 cc of lead subacetate and, after shaking, about 15 or 20 cc of saturated salt solution. Thereafter the process is the same as in the previous method except that the solution is acidified before extraction with 10 per cent hydrochloric acid.

These methods were tried out as follows: The benzoic acid was determined by method 1 in a sample of blackberry jam containing 0.15 per cent of benzoic acid added as sodium benzoate. The mixture filtered easily, giving a clear solution which was extracted without difficulty, forming no emulsion. The precipitate of calcium sulphate which formed on acidifying did not interfere with the extraction. The average percentages of recovery by this method on two sets of duplicate determinations were 103.8 and 105.0. Owing to the necessity for washing each portion of the extract three times the method is quite tedious. Samples of apple glucose jelly, orange marmalade, and apple and currant jelly, each containing 0.15 per cent of benzoic acid, were analyzed by the second method. The results were, respectively, 108.0, 96.0, and 92.6. Two of these three samples filtered very slowly.

Method 1 was then modified to permit the use of chloroform as the solvent. This modification is given on page 110 of this report. Determinations of benzoic acid by this method in blackberry jam, apple glucose jelly, orange marmalade, and currant jelly gave 98.2, 96.1, 97.3, and 96.1 per cent recovery, respectively. As there is no need of washing the chloroform solution after each extraction, a considerable saving of time is accomplished.

To determine the amounts of benzoic acid extracted by the successive portions of 70, 50, 40, and 30 cc of chloroform used, a sample of orange marmalade containing 0.187 per cent of sodium benzoate was extracted by the modified method just mentioned. A portion of the filtrate corresponding to 45 grams of the sample was extracted and the successive portions of chloroform were evaporated separately, dried, and titrated. The total recovery was 94.2 per cent. The first portion of 70 cc chloroform extracted 66.7 per cent of the benzoic acid; the second portion of 50 cc, 21.7 per cent; the third, 40 cc portion, 5.1 per cent, and the last 30 cc portion, 0.9 per cent

[1] U. S. Dept. Agr., Bureau of Chemistry Bul. 132, p. 149.

A number of other experiments gave similar results, the residue from the last 30 cc of chloroform never requiring more than 0.1 cc of twentieth-normal sodium hydroxid to neutralize it.

An attempt was then made to apply the ketchup method to the determination of sodium benzoate in dried codfish. Fifty grams of the sample were made alkaline with sodium hydroxid and diluted to 500 cc with saturated salt solution. After standing several hours, with frequent shaking, the clear solution was siphoned off and filtered. The solution filtered easily and gave a clear filtrate. On acidifying with sulphuric acid previous to extraction with chloroform a precipitate of protein matter resulted. This precipitate did not interfere with the extraction. The percentage recovery was only 80.6 per cent. The low recovery was due apparently to incomplete solution of sodium benzoate from the codfish when treated with salt solution. The preservative is perhaps held back by occlusion in the undissolved protein matter. It was then suggested that a preliminary extraction of the codfish with cold water be made before saturating with salt. In this way a large amount of protein matter goes into solution with the preservative. If the solution is then saturated with salt much of the protein matter is precipitated and may be filtered out while the benzoate remains in solution. On acidifying the salt solution, preparatory to extracting with chloroform, a further precipitation of protein occurs. This does not interfere with the extraction, however. A recovery of 96.2 per cent was obtained on the first trial of this method. The method is given in detail on page 111 of this report.

At the last meeting of the association a method suggested by Mr. Edmund Clark[1] was reported in which the chloroform extract of benzoic acid was titrated directly without evaporation. It is evident that if this method could be made to work successfully a considerable saving in time would be possible. Attempts to apply it have given high results, however, both in the hands of Mr. Clark and the referee. On two samples, one of apple butter, the other of codfish, the former analyst reported recoveries of 110.9 and 123.8 per cent, respectively. This may be due in part to the presence of a slight amount of hydrochloric acid taken up by the chloroform along with traces of emulsion. Such acid would be lost in the process of evaporation. That the high results are not wholly due to this cause is shown by the following experiment: 150 cc of saturated salt solution were treated with 7 cc of 1:5 hydrochloric acid and extracted with 70, 50, 40, and 30 cc portions of chloroform. The extract was transferred to a second separatory funnel, washed with 30 cc of water, treated with 100 cc of recently boiled water and a little phenolphthalein, and titrated with twentieth-normal sodium hydroxid until a faint pink color persisted after shaking. One and two-tenths cc of twentieth-normal sodium hydroxid corresponding to 9 mg of sodium benzoate were required to effect neutralization. Further work should be done upon this method.

As a result of the work just reported, the following method for the quantitative estimation of benzoic acid was sent to a number of collaborators, together with samples of raspberry jams, apple butter, and salt codfish, containing known amounts of preservative:

(b) Quantitative Estimation.

General Method of Preparation.

Grind in a sausage machine, if solid or semisolid, thoroughly mix the sample, and transfer a convenient quantity (about 150 grams) to a 500 cc graduated flask. Add enough pulverized sodium chlorid to saturate the water in the sample, render alkaline with sodium hydroxid or milk of lime, and dilute to the mark with a saturated salt solution. Allow to stand for at least two hours with frequent shaking and filter. If the sample contains large amounts of matter precipitable by salt solution it is advisable to follow a method similar to that given under "Salt or dried fish." When alcohol is present follow the method given under "Cider and similar products con-

[1] U. S. Dept. Agr., Bureau of Chemistry Bul. 132, p. 147.

taining alcohol." Where large amounts of fats are present it is well to make an alkaline extraction of the filtrate before proceeding as directed under Extraction and Titration. The following will illustrate the manner of applying the method to various classes of food products:

Special Methods of Preparation.

Ketchup.—To 150 grams of the sample add 15 grams of pulverized sodium chlorid and transfer the mixture to a 500 cc graduated flask, using about 150 cc of a saturated solution of sodium chlorid for rinsing. Make slightly alkaline to litmus paper with strong sodium hydroxid and complete the dilution to 500 cc with saturated salt solution. Allow to stand at least two hours with frequent shaking and then filter through a large folded filter. If any difficulty is experienced the mixture may be centrifuged or squeezed through a muslin bag before filtering.

Jellies, jams, preserves, and marmalades.—Dissolve 150 grams of the sample in about 150 cc of saturated salt solution and add 15 grams of pulverized sodium chlorid. Render alkaline to litmus paper with milk of lime. Transfer to a 500 cc graduated flask and dilute to the mark with saturated salt solution. Allow to stand at least two hours with frequent shaking, centrifuge if necessary, and filter through a large folded filter.

Cider and similar products containing alcohol.—Render 250 cc of the sample alkaline to litmus paper with sodium hydroxid and evaporate on the steam bath to about 100 cc. Transfer the sample to a 250 cc flask, add 30 grams of pulverized sodium chlorid, and shake until dissolved. Dilute to the original volume, 250 cc, with saturated salt solution, allow to stand at least two hours with frequent shaking, and filter through a folded filter.

Salt or dried fish.—Transfer 50 grams of the ground sample to a 500 cc flask with water. Make slightly alkaline to litmus paper with strong sodium hydroxid and dilute to the mark with water. Allow to stand at least two hours with frequent shaking and then filter through a folded filter. Pipette accurately as large a portion of the filtrate as possible (at least 300 cc) into a second 500 cc flask. Add 30 grams of pulverized sodium chlorid for each 100 cc of solution. Shake until the salt has dissolved and dilute to the mark with saturated salt solution. Mix thoroughly and filter off the precipitated protein matter on a folded filter.

Extraction and Titration.

Pipette a convenient portion of the filtrate (100 to 200 cc), obtained as above, into a separatory funnel. Neutralize the solution to litmus paper with hydrochloric acid (1:3) and add an excess of 5 cc of the same acid. In the case of salt fish a precipitation of protein matter usually occurs on acidifying, but the precipitate does not interfere with the extraction. Extract carefully with chloroform, using successive portions of 70, 50, 40, and 30 cc. To avoid emulsion shake each time cautiously (vigorous shaking is not necessary). The chloroform layer usually separates readily at the bottom of the funnel after standing a few minutes. If any emulsion forms it can be broken up by stirring the chloroform layer with a glass rod. If this is unsuccessful the emulsified portion may be drawn off into a second funnel and given one or two sharp shakes from one end of the funnel to the other. If this also fails the emulsion should be centrifuged for a few moments. As this is a progressive extraction great care must be taken to draw off as much of the clear chloroform solution as possible after each extraction, but under no circumstances must any of the emulsion be drawn off with the chloroform layer. If care is taken not to draw off any of the emulsion it is unnecessary to wash the chloroform extract.

Transfer the combined chloroform extract to a porcelain dish, rinsing the container several times with a few cubic centimeters of chloroform, and evaporate to dryness at room temperature in a current of dry air. (See note.) Dry the residue overnight (or until no odor of acetic acid can be detected in case the product is a ketchup) in a sulphuric acid desiccator. Dissolve the residue of benzoic acid in neutral alcohol (30 to 50 cc), add about one-fourth this volume of water, a drop or two of phenolphthalein solution, and titrate with twentieth-normal sodium hydroxid; 1 cc of twentieth-normal sodium hydroxid =0.0072 gram anhydrous sodium benzoate.

Note.—If a blast is convenient it is preferable to evaporate the whole extract at room temperature. For this purpose the following simple apparatus may be used: A wide-mouth salt bottle is fitted with a cork; a glass tube extends through the center of the cork to the bottom of the bottle, and its upper end is attached to the blast by a rubber tube. As many other glass tubes as convenient are passed through the cork around the central tube. These terminate just inside the cork, and outside the cork are bent outward and downward at an angle of about 45° C. The bottle is filled with calcium chlorid and by this means a current of dry air can be delivered to the dish

containing the extract. In the absence of a blast an electric fan may be used for evaporating the extract.

If it is impracticable to evaporate the chloroform spontaneously or by means of a blast it may be transferred from the separatory funnel to a 300 cc Erlenmeyer flask, rinsing the separatory funnel three times with 5 or 10 cc of chloroform. Distil very carefully to about one-fifth the original volume, keeping the temperature down so that the chloroform comes over in drops, not in a steady stream. Then transfer the extract to a porcelain evaporating dish, rinsing the flask three times with 5 or 10 cc portions of chloroform and evaporate to dryness spontaneously.

To avoid the error due to incomplete crystallization of the ordinary C. P. sodium benzoate the following procedure was used in making up the samples: Seven and one-half grams of pure benzoic acid were transferred to a 500 cc flask and partially dissolved in hot water. A few drops of phenolphthalein were added and then 60 cc of normal sodium hydroxid. The solution was finally neutralized exactly with tenth-normal sodium hydroxid. A slight excess of alkali was then added and the solution diluted to the mark. The percentage of benzoic acid actually present was calculated from the amount of sodium hydroxid used in the titration. Measured portions of this standard solution were added to the samples as desired. The samples were usually made up in 150 or 300 gram lots. A little less than this amount was weighed out, a measured quantity of the standard solution was added, the sample was then made exactly to the required weight, mixed very thoroughly, and transferred to a container. The results reported on these samples are shown in the following tables:

Determination of sodium benzoate in apple butter.

[Grams per 100 grams.]

Analyst.	Anhydrous sodium benzoate.			Analyst.	Anhydrous sodium benzoate.		
	Added.	Recovered.			Added.	Recovered.	
	Grams.	*Grams.*	*Per cent.*		*Grams.*	*Grams.*	*Per cent.*
C. Conover	0.147	0.134	91.2	W. W. Karnan	0.147	0.136	92.5
R. W. Clough	.147	.143	97.0	N. Hendrickson	.147	.122	83.0
F. F. Flanders	.147	.147	100.0	Do	.258	.262	[1] 101.8
W. C. Burnet	.147	.127	86.4	C. W. Clark	.147	.141	95.7
H. L. Lourie	.147	.142	96.6	Do	.147	.139	94.7
A. L. Knisely	.147	.147	100.0	Do	.177	.177	100.0
H. L. Jackson	.147	.145	98.6	S. H. Ross	.201	.204	101.4
A. G. Durgin	.147	.155	105.4				

[1] This sample was corrected by a blank determination made on the same sample of apple butter without addition of benzoate. The corrected result is 97.6 per cent.

Determination of sodium benzoate in codfish.

[Grams per 100 grams.]

Analyst.	Anhydrous sodium benzoate.			Analyst.	Anhydrous sodium benzoate.		
	Added.	Recovered.			Added.	Recovered.	
	Grams.	*Grams.*	*Per cent.*		*Grams.*	*Grams.*	*Per cent.*
C. Conover	0.353	0.332	94.1	A. G. Durgin	0.353	0.362	102.6
R. W. Clough	.353	.294	83.3	W. W. Karnan	.353	.347	98.3
F. F. Flanders	.353	.336	95.2	C. W. Clark	.353	.322	91.0
H. L. Lourie	.353	.336	95.2	Do	.588	.540	91.8
H. L. Jackson	.353	.209	59.2	Do	.588	.511	86.8
W. C. Burnet	.353	.126	35.7	A. L. Knisely	.588	.571	97.1
N. Hendrickson	.353	.287	81.3				

Determination of sodium benzoate in raspberry jam.

[Grams per 100 grams.]

Analyst.	Anhydrous sodium benzoate.			Analyst.	Anhydrous sodium benzoate.		
	Added.	Recovered.			Added.	Recovered.	
	Grams.	*Grams.*	*Per cent.*		*Grams.*	*Grams.*	*Per cent.*
C. Conover	0.177	0.134	75.7	C. W. Clark	0.177	0.144	81.6
W. C. Burnet	.177	.144	81.3	W. W. Karnan	.177	.138	78.0
C. W. Clark	.177	.223	126.5	H. L. Lourie	.179	.141	78.8
Do	.177	.146	82.6	N. Hendrickson	.181	.121	66.8
Do	.177	.146	82.6				

For some reason all the results reported on raspberry jam were low, the recovery usually being about 80 per cent. The reason for this has been sought in vain, but, as as has been stated before, samples of orange marmalade, blackberry jam, and apple jelly gave practically 100 per cent recovery. It will be seen that of 15 reports received on the sample of apple butter, 1 had a percentage recovery of 105.4 per cent; 2 between 100 and 102 per cent; 7 between 95 and 100 per cent; 3 between 90 and 95 per cent; and 2 between 83 and 90 per cent. Of 13 results reported on the codfish samples, 1 was 102.6 per cent; 4 were between 95 and 100 per cent; 3 between 90 and 95 per cent; 3 between 80 and 90 per cent; and 2 very low.

At the 1908 meeting of the association some work[1] was reported on a method depending on the precipitation of benzoic acid as silver benzoate. Attention should be called to this method again for the reason that it is valuable as a check on the results obtained by the method just given. With proper care it is capable of giving excellent results. As originally published the method directed the use of aldehyde-free alcohol for dissolving the sodium-benzoate residue and for making up all reagents. This precaution may be dispensed with. Great care must be taken not to add an excess of sodium hydroxid in neutralizing the benzoic-acid residue, as the presence of any free alkali will seriously affect the results. The chief disadvantage of the method is the very long time required for filtration when a considerable amount of precipitate is present. The method as used at present is as follows:

After titrating the benzoic acid, evaporate to dryness at a gentle heat. Redissolve the residue in absolute alcohol, filter off any residue not soluble in the alcohol, and precipitate as silver benzoate by adding 10 or 15 cc of the silver-nitrate reagent (prepared by dissolving to saturation, pure, pulverized, silver nitrate in absolute alcohol, and filtering). Filter at once on a small asbestos gooch prepared to filter quickly with a very thin mat. Wash first with a few cubic centimeters of absolute alcohol and finally with a few cubic centimeters of ether. Dry in the water oven for a short time until the ether is driven off; cool and weigh.

Modification of Mohler's Test for Benzoic Acid.

The following modification of Mohler's[2] test for benzoic acid by von der Heide and Jakob[3] has appeared during the past year.

Take up the residue of pure benzoic acid in 1 to 3 cc of third-normal sodium hydroxid and evaporate to dryness. To the residue, add 5 to 10 drops of concentrated sulphuric acid and a small crystal of potassium nitrate. Heat for 10 minutes in glycerol bath at 120° to 130° C., or for 20 minutes in a boiling water bath. This causes the formation of meta-di-nitro-benzoic acid. In no case must the temperature exceed 130° C. After cooling, add 1 cc of water and make decidedly ammoniacal; boil the solution, to break up any ammonium nitrite which may have been formed. Cool and

[1] U. S. Dept. Agr., Bureau of Chemistry Bul. 122, p. 74; also W. E. Hillyer, J. Ind. Eng. Chem., 1 (8): 538.

[2] Bul. soc. chim. 1890, 3 (3): 414; U. S. Dept. Agr., Bureau of Chemistry Bul. 107, Revised, p. 181.

[3] Zts. Nahr. Genussm., 1910, 19 (3): 137, and Chem. Abst. 1910, 4 (11): 1523.

add a drop of fresh colorless ammonium sulphid, without allowing the layers to mix. A red-brown ring indicates benzoic acid. This is due to the formation of ammonium meta-di-amido-benzoic acid. On mixing, the color diffuses through the whole liquid; on heating it finally changes to greenish yellow, owing to the decomposition of the amido acid. This furnishes a means of distinguishing benzoic acid from salicylic or cinnamic acids. Both the latter form amido compounds, which are not destroyed by heating. The presence of phenolphthalein interferes with this test.

This method has been tried by R. W. Hilts and the referee. A solution containing known amounts of benzoic acid was used and the method followed exactly, performing the nitration by heating for 20 minutes in boiling water. Mr. Hilts makes the following comments:

I found the method to give a beautifully distinct reaction with 0.5 mg of benzoic acid, and moreover the method seems to be very reliable and certain, since conditions are under good control. I summarize some of these tests as follows:

2.0 mg of benzoic acid—very deep brownish red tint.
1.0 mg of benzoic acid—deep brownish red tint.
0.5 mg of benzoic acid—very distinct brownish red tint.
0.1 mg of benzoic acid—faint brownish red tint.

The method described seems to be very superior to the original Mohler's test as given in Bulletin 107, Revised. We have tried it successfully in this laboratory on sublimates obtained from jams. The small amount of material necessary for the test is, of course, a great advantage.

Similar results were obtained by the referee. It was found that a very clear test was obtained on the residue extracted by chloroform from a dark beer to which sodium benzoate was added. A red brown ring very similar to that given by benzoic acid is produced by salicylic and cinnamic acids and by phenolphthalein. Three-eighths of a milligram of salicylic acid gives a very strong red-brown color which develops more slowly than in the case of benzoic acid. Cinnamic acid gives a faint test with 0.75 mg; with this acid the odor of benzaldehyde is usually noticeable on neutralizing with ammonia. Three drops of a 0.1 per cent solution of phenolphthalein produce a strong coloration. In all cases, however, on warming the color diffuses throughout the solution remaining brown or dark red, according to the concentration, whereas the solution obtained from benzoic acid changes to a greenish yellow. It is to be remembered that this test is applicable only where the benzoic acid residue is reasonably pure, as the presence of any large amount of organic matter will interfere with the test.

Determination of Total Sulphurous Acid.

The method given in Bulletin 107 for the determination of total sulphurous acid by distillation directs that the distillate be collected in a standard iodin solution and the amount of iodin reduced be determined by titration. This method has been found by many experimenters to be faulty for the reason that reducing substances other than sulphur dioxid frequently pass over in the distillate. It has been found best to determine the sulphuric acid gravimetrically as barium sulphate. Bromin water is usually used as the oxidizing agent instead of iodin solution.

Recommendations.

In view of the work just reported it is recommended—

(1) That in Bulletin 107, Revised, page 181, under "(2) Benzoic acid—(a) Qualitative determination," the first sentence be changed as follows: Separate the benzoic acid as directed for salicylic acid or by the method given under "(b) Quantitative estimation."

(2) That on page 181, for "(2) Second method—Mohler's method," the modification by von der Heide and Jakob just given be substituted.

(3) That the method given on page 181, under "(b) Quantitative estimation" be dropped and the method given on pages 110 to 111 of this report be substituted as a provisional method.

(4) That the Hillyer method for the determination of benzoic acid as silver benzoate be tried by the association.

(5) That further study be made of the possibility of making a direct titration of benzoic acid on the chloroform extract.

(6) That on page 187, the method given under "(b) Determination of total sulphurous acid, (1) First method (Distillation method)" be replaced by the following:

(1) FIRST METHOD (DISTILLATION METHOD).

Distil from 20 to 100 grams of the sample (adding recently boiled water if necessary) in a current of carbon dioxid, after the addition of about 5 cc of a 20 per cent solution of a glacial phosphoric acid, until 150 cc have passed over. Collect the distillate in about 100 cc of nearly saturated bromin water. Allow the end of the condenser to dip below the surface of the liquid in the receiver. The method and apparatus may be simplified without material loss in accuracy by omitting the current of carbon dioxid, adding 10 cc of phosphoric acid instead of 5 cc, and dropping into the distilling flask a piece of sodium bi-carbonate weighing not more than a gram, immediately before attaching the condenser. The carbon dioxid liberated is not sufficient to expel the air entirely from the apparatus but will prevent oxidation to a large extent. When the distillation is finished, boil off the excess of bromin, dilute the solution to about 250 cc, add 5 cc of hydrochloric acid (1 part of the concentrated acid to 3 of water), heat to boiling and precipitate the sulphuric acid with a 10 per cent solution of barium chlorid. Boil for a few minutes longer, allow to stand overnight in a warm place, filter on a weighed Gooch crucible, wash with hot water, ignite at a dull red heat and weigh as barium sulphate.

EFFECT OF NITRATES AND NITRITES ON THE TURMERIC TEST FOR BORIC ACID.

By T. M. PRICE and E. H. INGERSOLL.

This brief paper is merely to report certain observations made by the writers concerning the effect of nitrates and nitrites on the turmeric test for boric acid. In dealing with certain solutions containing nitrates, it was found that when these solutions were tested for boric acid by allowing them to evaporate on the steam bath in contact with a strip of turmeric paper the turmeric paper was often bleached white. In the literature on this subject were found statements to the effect that nitrates interfered with the turmeric test for boric acid. Low,[1] however, claims that nitrates will not interfere with this test if the turmeric paper is dipped in the solution to be tested and then allowed to dry in the air or in vacuo. This statement led to the making of experiments to determine why the nitrates interfered in the one case and not in the other. From the results of these experiments, it was learned that the nitrates, as such, did not interfere with the turmeric test; but when the solutions of nitrates containing hydrochloric acid were evaporated on the steam bath, nitrites were formed and it was suspected they were the interfering agent. Experiments were then made to determine whether nitrites would interfere with the turmeric test for boric acid if the paper was dried in the air, and the results showed that nitrites had a very marked effect on the turmeric test even when the paper was dried in the air or in vacuo. A solution of boric acid containing 0.01 per cent of potassium nitrite gave a decidedly paler pink color to the turmeric paper than the same strength solution of boric acid free from nitrites, whereas a solution containing 0.1 per cent of potassium nitrite completely inhibited the production of the intense pink color that a 0.3 per cent boric acid solution should give to turmeric paper under ordinary conditions.

It may be readily seen that some modification of the turmeric test was necessary before it could be relied upon to detect small quantities of boric acid in mixtures containing nitrites. To obviate the effect of the nitrites on the turmeric paper, a number of modifications of the turmeric test were tried. By adding organic matter to a boric acid solution containing nitrites, rendering it alkaline, evaporating to dry-

[1] J. Amer. Chem. Soc., 1906, 28 (7): 807.

ness and burning, the boric acid salt will remain in the ash and the turmeric test is not interfered with, as the nitrites are destroyed on burning. This method, however, was not entirely satisfactory, as it necessitated evaporation, which lengthened the method considerably, and the mixture also spattered badly when burned, usually resulting in the loss of a considerable portion of the sample. A number of other modifications of the turmeric test were tried but none was found satisfactory. The reaction which is often utilized to remove nitrous acid from a solution by the addition of urea was finally attempted, with excellent results.

The method as modified and finally adopted for detecting boric acid in solutions containing nitrites is as follows:

Acidify 9 cc of the solution to be tested with hydrochloric acid, add 1 cc of concentrated hydrochloric acid containing 5 grams of urea per 100 cc, shake the mixture, and allow to stand for five minutes. Immerse turmeric paper in this solution momentarily, hang up, and allow to dry in the air.

The results of the experiments show that as much as 0.3 per cent of potassium nitrite may be present in a solution containing 0.01 per cent of boric acid without any interference whatever with the test when urea is employed as described.

On motion by Mr. Frear it was ordered that all recommendations affecting the adoption of either provisional or official methods should be voted on one at a time, but that all recommendations on one subject concerning lines of work or proposed investigations might be approved by a single vote.

On motion by Mr. Bigelow a committee was appointed to draft suitable resolutions in regard to the death of Albert E. Leach, for many years an honored member of the association. The president named Messrs. Wiley, Lythgoe, and Winton on this committee.

REPORT OF COMMITTEE C ON RECOMMENDATIONS OF REFEREES.

Food Adulteration.

By A. L. Winton, *Chairman.*

Spices.

It is recommended—

(1) That on page 168 of Bulletin 107, Revised, under "9. Crude fiber," the following words be inserted at the end of the paragraph: "; the fiber, however, should finally be washed successively with alcohol and ether until all fat is removed."

Carried.

(2) That a comparative study be made of the determination of fiber with and without preliminary drying and extraction of fat.

Carried.

(3) That the method for the detection of olive oil in paprika, submitted by the referee, be made provisional (see p. 81).

Carried.

(4) That a further study be made of the chemical characteristics of paprika extract with a view to detecting added foreign oils other than olive oils, and of drying the ether extract in vacuo and in hydrogen.

Carried.

Separation of Meat Proteids.

It is recommended—

(1) That a special study be made of the hydrolytic cleavage products of the nitrogenous bodies in beef extracts in order to determine what bodies resist the Kjeldahl digestion when a large sample of beef extract is used.

Carried.

(2) That cooperative tests with the Kjeldahl method as applied to beef extracts be made with a view to determining the best conditions for complete digestion.

Carried.

(3) That cooperative work on the separation of meat proteids in beef extracts be continued.

Carried.

Separation of Vegetable Proteids.

It is recommended—

(1) That in the method for the determination of salt-soluble nitrogen all words from "Place filtrate in Kjeldahl digestion flask" to end of paragraph be omitted and replaced by "and determine nitrogen by the Kjeldahl or Gunning method."

This recommendation, which refers to the method submitted by the referee for study (p. 150), was carried.

(2) That the influence of the strength of salt solutions upon the proportion of nitrogen dissolved be made a matter of study.

Carried.

(3) That the work of separating the various proteids be carried out in conjunction with actual baking trials.

Carried.

Fats and Oils.

It is recommended—

(1) That the method submitted by the referee (p. 88) for the detection of fish oil in the presence of vegetable oils be adopted as provisional.

Carried.

Organic and Inorganic Phosphorus in Foods.

It is recommended—

(1) That the magnesia mixture method of Forbes, the barium chlorid method of Siegfried and Singewald, and the neutral ammonium molybdate method of Hart and Andrews as modified by Emmett and Grindley, for the separation and estimation of inorganic and organic phosphorus in foods be further studied with a view to determining their accuracy (see report, p. 142).

Carried.

Dairy Products (Adulteration of).

It is recommended—

(1) That the line of work recommended by the referee in 1909 be continued (Bul. 132, pp. 131 and 166).

Carried.

Preservatives.

It is recommended—

(1) That in Bulletin 107, Revised, page 181, under "2. Benzoic acid, (a) Qualitative determination," the first sentence be changed to read as follows: "Separate the benzoic acid as directed for salicylic acid, or by the method given under (b) Quantitative estimation."

Carried.

(2) That in Bulletin 107, Revised, page 181, for "(2) Second method (Mohler's method)" substitute the modification by von der Heide and Jakob. (See p. 113; modify the first line to read as follows in order to follow section (a) properly: "Add to the water solution prepared as described under (a) from 1 to 3 cc, etc.")

Carried.

(3) That the method given on page 181, Bulletin 107, Revised, under "(b) Quantitative estimation," be dropped and the methods given in the referee's report (pp. 110–112) be substituted as a provisional method.

Carried.

(4) That the Hillyer [1] method for the determination of benzoic acid as silver benzoate be tried by the association.

Carried.

(5) That further study be made of the possibility of making a direct titration of benzoic acid in the chloroform extract.[2]

Carried.

(6) That in Bulletin 107, Revised, page 187, the method given under "(b) Determination of total sulphurous acid, (1) First method (Distillation method)" be replaced by the method given in the referee's recommendations, page 115.

Carried.

Cocoa and Cocoa Products.

It is recommended—

(1) That the method tried this year for the determination of sucrose and lactose be substituted as provisional, for that given on page 256 of Bulletin 107, Revised, and that the alternate procedure suggested for the first part of the method be further studied.

Carried. (See p. 101.) The alternate procedure to be substituted for the method to the point at which the direct polariscope reading is made, reads as follows:

Transfer 26 grams to a bottle or flask of suitable size, add 100 cc of water, cork the bottle and place in steam bath for 20 minutes, releasing the pressure occasionally during the first 5 minutes of heating. Twice during the 20 minutes shake the container thoroughly so as to completely emulsify the chocolate solution. Remove from steam bath, cool to room temperature, add 10 cc basic lead acetate solution, mix and filter.

(2) That the method tried this year for the determination of fat be further tested to determine whether serious loss of ether takes place in a warm atmosphere, and if so to devise a method of overcoming the difficulty.

Carried. (See p. 103.)

(3) That the referee investigate methods for determining the amount and character of the milk solids in milk cocoas and chocolates.

Carried.

Tea and Coffee.

It is recommended—

(1) That the Gorter method for the determination of caffein in coffee be adopted as provisional in the place of the Hilger and Fricke method (Bulletin 107, Revised, p. 153).

Carried. (The association first recommended further study of this method but upon a supplementary report by Committee C it was made provisional. See Chemistry Bulletin 132, p. 135, for statement of method except that it was found necessary to pass the solution through a moistened filter paper in addition to the cotton plug in order to obtain a perfectly clean filtrate.)

(2) That the method of Lendrich and Nottbohm for the determination of caffein in coffee be further studied.

Carried. (See p. 107 of referee's report.)

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[1] Statement of original Hillyer method is given on page 74 of Bureau of Chemistry Bulletin 122, or J. Ind. Eng. Chem. 1909, 1:538. The method as originally published has been somewhat modified. The use of aldehyde-free alcohol may be dispensed with throughout and it is unnecessary to saturate the alcohol with silver benzoate in any part of the process. The benzoic acid residue must be exactly neutralized before precipitation and the use of an alcoholic solution of alkali is not necessary.

[2] U. S. Dept. Agr., Bureau of Chemistry Bul. 132, p. 147.

(3) That the subject of tea be studied during the coming year.

Carried.

Cereal Products.

It is recommended—

(1) That the associate referee on cereal products be instructed to devote special attention to methods for analyzing and testing wheat and flour.

Carried. (Included in supplementary report of Committee C. Attention was called to the fact that no methods for cereal products are given in Bulletin 107, Revised, and that milling and baking tests were also needed.)

Water in Foods.

It is recommended—

(1) That the vacuum method for the determination of moisture in foods be further studied as to its special applicability to other food products, especially those containing volatile oils, and also to determine the influence of the method of moisture determination upon the subsequent determination of the ether-soluble substance (fat).

Carried. (See Bul. 122, p. 219, and Bul. 132, p. 150.)

Reference Tables.

The following recommendation was introduced by P. H. Walker and referred to Committee C:

That the tables on pages 66 (Comparison of specific gravities, degrees Brix and degrees Baumé), 67 (Correction for the readings of the Brix spindle when the reading is made at other than the standard temperature 17.5°), and 221 to 224 inclusive (Relation of Brix, specific gravity, and Baumé, and Correction for the readings of Balling's saccharometer, on account of temperature) be omitted from Bulletin 107, Revised, and that the tables, No. 7 (Temperature corrections to saccharometer readings, standard at 20° C.), No. 8 (Density of solutions of cane sugar at 20° C.), No. 11 (Degrees Baumé corresponding to specific gravities at 60° F. (15.56° C.) greater than 1), No. 12 (Degrees Baumé corresponding to specific gravities at 60° F. (15.56° C.) less than 1), and No. 13 (Conversion of density basis), from Circular 19 of the Bureau of Standards, be inserted.

The committee recommended that the tables specified be presented to the association for the consideration of the members with a view to taking final action on the suggested substitution in 1911, which recommendation was adopted. Inasmuch as the tables may be obtained by any member of the association by applying to the Bureau of Standards for Circular 19, they will not be reprinted. The following reasons for making the substitution, as presented by Mr. Walker, are given for the information of the association:

Formerly the Brix spindle was made to read at 17.5° C. and the tables given in Bulletin 107, Revised, are based on this standard, the corresponding specific gravity of a sugar solution being at $\frac{17.5°\ C.}{17.5°\ C.}$. The degrees Baumé given in the tables of Bulletin 107, Revised, do not refer to the American standard and can not be relied upon as being accurate with Baumé hydrometers used in this country. The standard Baumé spindles are intended to be used at 60° F. The present standard temperature for calibrating Brix spindles is $\frac{20°\ C.}{4°\ C.}$. This is the standard in this country and is also the standard which has been recommended by the International Congress of Applied Chemistry. Any Brix spindles which are sent to the Bureau of Standards for testing will be tested according to Table No. 8 of Bureau of Standards Circular No. 19. Because of the different temperatures at which the spindles are calibrated it is not feasible to convert degrees Brix into degrees Baumé, and tables showing this conversion should be eliminated from Bulletin 107, Revised. It would, however, probably be useful to have available a correct table giving values of degrees Baumé in specific gravity, and Tables Nos. 11 and 12 of Bureau of Standards Circular No. 19 are the American official tables for this purpose.

Baking Powder.

It is recommended—

(1) That the kind and strength of acid used in determining carbon dioxid in baking powders be further studied.

Carried.

Flavoring Extracts.

It is recommended—

(1) That the method of determining vanillin, coumarin, and normal lead number in one weighed portion be studied next year.

Carried. This process as described by Winton and Lott is described in the Proceedings of the association for 1909 (Bul. 132, p. 110). Since that time Winton and Berry have found that the amount of lead precipitated is materially affected by the time of standing, after adding the standard lead acetate solution, and by the temperature of the solution during this standing. After numerous experiments they recommend standing for 18 hours (overnight) at from 37° to 40° C. The desired temperature can be secured by keeping the solutions contained in the 100 cc flasks in a bacteriological incubator or in a water bath provided with a constant temperature regulator. Proceeding in this manner they find that the minimum normal lead number for extracts prepared according to the U. S. Pharmacopœia is 0.40.

(2) That the text on page 68 of the referee's report be substituted for all material under the heading "4. Determination of vanillin, coumarin, and acetanilid," Bulletin 107, Revised, pages 156 to 158.

Carried.

(3) That the word "basic," under 11 (b), third line, Bulletin 107, Revised, page 159, be omitted.

Carried.

(4) That Woodman and Newhall's test for caramel be further investigated. (See referee's report, p. 69.)

Carried.

(5) That the headings "Lemon extract," and "4. Lemon oil," on pages 159 and 160, Bulletin 107, Revised, be changed to read "Lemon and orange extracts," and "4. Lemon and orange oils."

Carried.

(6) That the text on page 69 of the referee's report be substituted for "(a) By polarization (Mitchell)," page 160, Bulletin 107, Revised.

Carried.

(7) That the last sentence under "(b) By precipitation," on page 160, be omitted.

Carried.

(8) That the paragraph headed "5. Refraction of precipitated oil," page 160, be omitted.

Carried.

(9) That the heading of the provisional method "Determination of citral in lemon extract," adopted in 1908 (see Bul. 122, p. 32, or Cir. 43, p. 10), be changed to read "Determination of total aldehydes in lemon and orange extracts."

Carried.

(10) That the Hiltner method for the determination of citral in lemon and orange extracts be adopted as provisional.

Carried. (See p. 70 for statement of method.)

(11) That under "10. Detection of coloring matter," page 161, Bulletin 107, Revised, insert the methods on lemon and orange peel color and on turmeric, as given in the referee's report, page 71.

Carried.

(12) That the methods for the examination of lemon and orange oils, outlined on page 72 of the referee's report, be provisionally adopted.

Carried.

(13) That the methods for the examination of almond extract, given on page 73 of the referee's report, be provisionally adopted.

Carried.

(14) That the methods for the examination of cassia, cinnamon, and clove extracts, given on page 75 of the referee's report, be provisionally adopted.

Carried.

(15) That the methods for the examination of ginger extract (Par. 1 to 3), as given on page 75 of the referee's report, be adopted as provisional.

Carried.

(16) That the tests given on page 75 for the detection of capsicum in ginger extract (Par. 4), be further studied.

Carried.

(17) That the methods for the examination of nutmeg and wintergreen extracts be further studied.

Carried.

(18) That the Howard method for the examination of peppermint extract be adopted as provisional.

Carried.

The association adjourned until Saturday morning at 9 o'clock.

THIRD DAY.

SATURDAY—MORNING SESSION.

Mr. Haywood submitted a supplementary report on behalf of Committee A concerning a recommendation under nitrogen, which was adopted (see p. 46).

President Withers introduced a resolution concerning a journal of agricultural research and calling for a special committee in regard to the matter. The resolution was referred to the committee on resolutions.

REPORT ON VEGETABLES.

By John Phillips Street,[1] *Associate Referee.*

The work of the referee this year has not been so much a comparison of methods as the securing of abundant analytical data, generally by means of well-known methods, on which data it was hoped a correct judgment as to the purity of the vegetable product might be based. For this purpose 111 samples of canned peas and 74 samples of ketchup have been analyzed with considerable completeness in my laboratory. No cooperation from other laboratories was requested. The detailed analyses of these samples will not be given in this report, but will be found in full in the Connecticut Station report. The report as here given will consist chiefly of a summary of the results obtained, with the conclusions drawn from these results.

Canned Peas.

In the examination of canned peas considerable attention was given to physical data in addition to chemical analysis.

One hundred and eleven samples were examined, representing practically all of the brands on the Connecticut market. Besides making a quite complete examination of the pea liquor and the drained peas separately, the following purely physical data were obtained: Weight of drained peas, weight of liquor, weight relation of peas to liquor, escape of gas on opening, discoloration or corrosion of the can, presence of solder in the peas, appearance of liquor, completeness of fill, color and consistency of the peas, prominence of cotyledons, weight of 100 drained peas, grading for size by means of appropriate sieves, and grading for quality by means of salt solutions of differing densities. These will be considered briefly before taking up the chemical data obtained.

[1] Credit for the analytical work herein reported is due to E. M. Bailey, C. B. Morison, R. B. Roe, and C. E. Shepard, who rendered valuable assistance.

PHYSICAL DATA

Weight of samples.

Data.	Maximum.	Minimum.	Average.
	Grams.	*Grams.*	*Grams.*
Weight of can and contents	723	380	672
Weight of peas and liquor	623	315	570
Weight of drained peas	455	211	364
Weight of liquor	305	101	206
Per cent of liquor, by weight	49.7	27.0	36.1

The variations in the weight of drained peas of samples, whose branding indicated a specific size, was also studied.

Variations in weight of drained peas.

Grade.	Maximum.	Minimum.	Average.
	Grams.	*Grams.*	*Grams.*
Petits pois	380	211	292
Extra sifted	398	261	350
Sifted	423	243	368
Early June	412	309	373
Marrowfat	455	371	400
Telephone	412	354	383
Miscellaneous	424	270	373

According to Bitting, "the average fill of a can is such that after processing there will be 14 ounces of peas (400 grams) and 7¼ ounces (200 grams) of liquor." These figures of course only apply to No. 2 cans. Of the 92 samples packed in cans of this size, 56 contained less than 385 grams of drained peas, 31 between 385 and 415 grams, and 5 over 415 grams. That is, 61 per cent had a tendency toward short weight, 34 per cent were normal, and 5 per cent contained too much peas for the liquor. In three samples the liquor made up 50, 44, and 42 per cent of the total weight, while in one it made up only 27 per cent.

Escape of gas on opening.—In 10 samples there was no escape of gas, in 61 slight, in 36 considerable, and in 4 much.

Discoloration or corrosion of can.—In 10 there was none, in 52 slight, in 46 considerable, and 3 very marked discoloration.

Appearance of liquor.—The liquor was perfectly clear in no case. In 10 it was slightly cloudy, in 63 cloudy, in 33 thick, and in 5 very thick and pasty.

Completeness of fill.—According to Bitting, a can is well filled when the contents are within ⅜ inch of the cap, and the peas just covered with liquor. In 7 the contents were 0.1 inch from the cap; in 6, 0.2 inch; in 21, 0.3 inch; in 47, 0.4 inch; in 25, 0.5 inch; in 4, 0.6 inch; and in 1, 0.7 inch. Thirty samples, or 27 per cent, showed over 0.4 inch of empty can. The shortage was sometimes in peas, sometimes in liquor, sometimes in both.

In 6 samples the peas were 0.2 inch above the liquor; in 1, 0.1 inch; in 6 the peas and liquor were coincident; in 14 the liquor was 0.1 inch above; in 19, 0.2 inch; in 27, 0.3 inch; in 15, 0.4 inch; in 16, 0.5 inch; in 3, 0.6 inch; and in 1 each, 0.7, 0.8, 0.9, and 1.3 inch above. In 13 samples the liquor was insufficient, in 31 excessive, and in 7 markedly excessive.

Color of peas.—The color ranged from bright green to yellow, but was generally satisfactory. The coppered samples had an unnaturally bright-green color, and some of the more mature peas were distinctly yellow.

Consistency of peas.—In consistency the peas ranged from soft and mushy to hard. In some samples there were many broken peas, suggesting the probable use of soaked peas.

Prominence of cotyledons.—In 42 samples the cotyledons were not prominent, in 56 prominent, and in 13 of varying prominence.

Weight of 100 drained peas.—These weights ranged from 16 to 83 grams, with an average of 40 grams. The average weight of samples labeled petits pois was 24; extra fins, 25; sifted, 35; early June, 41; marrowfat, 46; and telephone, 56 grams.

Grading for size.—One hundred peas were passed through a special set of sieves having round holes $\frac{9}{32}$, $\frac{10}{32}$, $\frac{11}{32}$, $\frac{12}{32}$, and $\frac{13}{32}$ of an inch in diameter. It is recognized that during processing the peas increase somewhat in weight and size and that this test is not absolute, but merely indicative. In 72 of the 111 samples the label indicated a standard size, namely, 13 No. 1; 6 No. 2; 23 No. 3; 22 No. 4; 2 No. 5; and 6 No. 6. The proper grading by size of the whole number would be 12 No. 1; 20 No. 2; 36 No. 3; 36 No. 4; 5 No. 5; and 2 No. 6. Of the samples labeled a definite size 23 were true to size, 34 were smaller, and 15 were larger, judging from the majority of peas of any one size. All those marked early June, marrow, or telephone were equal to or better than the grade claimed. Only 46 per cent of the No. 1, 67 per cent of the No. 2, and 74 per cent of the No. 3 were of as good grade as claimed. The maximum percentages of the six grades were 100, 94, 80, 88, 66, and 60, respectively, the minimum in all cases zero, and the averages 14, 20, 29, 28, 7, and 2, respectively.

Grading for quality.—One hundred peas were placed in salt solutions of 1.04 and 1.07 specific gravity, and the number counted which floated in the first, those which sank in the first and floated in the second, and those which sank in the second. The figures obtained were very unsatisfactory and in most cases conveyed little useful information. This method, which is of great value in grading the fresh peas, seems to require solutions of greater specific gravity than those used in this investigation, when canned peas are to be examined, and for obvious reasons is of doubtful value in examining laboratory samples.

CHEMICAL EXAMINATION.

The pea liquor and drained peas.

The pea liquor should consist chiefly of water, salt, and sugar. Sugar is frequently used for the purpose of giving "a weak, insipid, sugarless pea some semblance of quality, also to make the smooth pea as sweet as the sweet wrinkled variety."

The usual practice of the housewife is to drain off the liquor immediately on opening the can, and throw it away. Some canners, recognizing the amount of extracted nutriment in the liquor, recommend its use in preparing peas for the table, but generally it is entirely wasted.

In the samples examined the liquor made up from 27 to 49.7 (average, 36.1) per cent of the total weight. It seemed important to determine the amount of nutriment in this liquor, as from the weight standpoint 4.9 cents of the average cost, 13.5 cents, is attributable to the liquor.

Analysis of pea liquor.

Determinations.	Maximum.	Minimum.	Average.
	Per cent.	*Per cent.*	*Per cent.*
Water	96.27	89.32	93.33
Ash	2.16	.49	1.15
Protein (N×6.25)	3.04	.66	1.55
Sucrose	5.21	.00	2.44
Undetermined, chiefly starch	5.40	.21	1.53
Sodium chlorid	1.73	.23	.81
Sodium chlorid-free ash	.64	.19	.34

The composition of the liquor was exceedingly variable. No striking differences were shown between the liquors of peas of the different grades, although in the petits pois the percentages of ash, protein, and starch were somewhat lower than in the more mature peas. The solids ranged from 3.73 to 10.68 per cent, made up on the average of 23 per cent of protein, 37 per cent of sugar, 23 per cent of starch, 5 per cent of pea ash, and 12 per cent of salt.

The following tabulation shows the average composition of the solids of the liquor and of the drained peas per can in the 111 samples.

Average data on 111 samples.

Determinations.	206 grams of liquor contain—		364 grams of drained peas contain—	
	Grams.	*Per cent of total.*	*Grams.*	*Per cent of total.*
Ash	2.37	38	3.86	62
Protein	3.19	16	16.82	84
Carbohydrates	8.18	15	47.32	85
Fat	.....	.....	1.67	100
Total solids	13.74	16	69.67	84

That is, 16 per cent of the total solids is represented in the discarded liquor. This, however, does not necessarily mean that much loss of pea substance, for sugar is often added for sweetening purposes and salt for seasoning. The 10 per cent loss of starch and 16 per cent loss of protein are, however, actual losses of pea substance and represent a distinct waste of food. These losses are due in part to methods of canning, too little liquor increasing mushiness in the peas, and consequently causing a thick, cloudy liquor. Even with the best methods, however, the liquor represents considerable waste, and the processes should be so improved as to eliminate or minimize the odor of the liquor, which is disagreeable to many, and insure a nearly clear liquor free of excessive starch. The solubility of a portion of the pea protein in water and weak sodium chlorid solutions offers a chemical problem more difficult to solve. If, however, the present objectionable features of the liquor can be removed and its use made admissible, this loss of protein becomes entirely a question of household economics.

The liquor was not examined for metallic contamination, for while it is recognized that certain of the tin and copper salts may be present in the liquor the fact that the liquor is rarely used at present for food makes their determination of relative unimportance.

Average composition of drained peas and of liquor (111 samples).

Determinations.	Drained peas.		Liquor, original.	Peas and liquor.	
	Original.	Water-free.		Original.	Water-free.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Water	80.86	.....	93.33	85.37	.....
Ether extract	.46	2.40	.....	.29	1.98
Fiber	1.77	9.25	.....	1.13	7.72
Ash	1.06	5.54	1.15	1.09	7.45
Protein	4.62	24.14	1.55	3.51	24.00
Nitrogen-free extract	11.23	58.67	3.97	8.61	58.85
Nitrogen	.74	3.86	.25	.56	3.83
Sodium chlorid	.58	3.03	.81	.66	4.51
Pea ash	.48	2.51	.34	.43	2.94

By comparing these averages with the average analyses of 20 samples of fresh peas by Dubois [1] it is evident that during the process of canning the peas take up considerable water, on the average about 8 per cent. The most important changes, however, are found in the ash and protein. While the total ash has increased from 3.61 per cent in the fresh peas to 5.54 per cent in the drained peas, water-free basis, this increase is due to the added salt, 3.03 per cent, the true pea ash showing a loss of 1.10 per cent. The protein has decreased from 28.13 to 24.14 per cent, the loss chiefly occurring during the washing and blanching of the peas.

The range of the different ingredients in the drained peas was as follows:

Limits of composition on drained peas examined.

Determinations.	Original substance.		Water-free.	
	Minimum.	Maximum.	Minimum.	Maximum.
Water	72.83	90.46	.....	.....
Ether extract	.14	.85	0.77	4.24
Fiber	.94	2.08	7.12	11.91
Ash	.52	1.69	2.92	9.30
Protein	2.52	6.45	18.43	30.86
Sugar	.34	5.18	1.37	28.71
Starch	2.04	15.65	21.38	59.78
Nitrogen-free extract	4.75	18.58	49.75	68.38
Sodium chlorid	.09	1.12	.46	6.67

In 72 samples the labels indicated a distinct classification based on size. The following tabulation gives the average composition of the water-free material of the drained peas, based on the label grade.

Percentage composition of drained peas (water-free) based on label grade.

Grade of peas.	Dry matter per can.	Fat.	Fiber.	Ash.	Protein.	Nitrogen-free extract.	Sodium chlorid.	Sugar.	Starch.	Undetermined.
	Grams.									
Petits pois	45	2.01	10.44	6.98	22.86	57.71	4.25	13.82	36.54	7.35
Petits pois extra fins	46	1.97	11.43	6.46	27.96	52.18	3.54	12.38	31.50	8.30
Petits pois fins	48	1.27	11.37	6.30	22.73	58.33	3.66	7.88	42.43	8.02
Extra fins, or extra sifted	45	2.51	10.85	6.17	24.92	55.55	3.60	17.27	29.09	9.19
Early June extra sifted	59	2.42	9.13	6.41	26.02	56.02	3.63	12.48	34.69	8.85
Sifted or fins	70	2.32	9.36	5.53	23.53	59.26	3.02	15.15	37.41	6.70
Early June sifted	86	1.80	8.43	5.06	22.67	62.04	2.83	8.26	48.70	5.08
Early June	84	2.09	8.54	5.39	23.56	60.42	2.97	7.32	46.35	6.75
Marrow sifted	84	2.60	9.59	5.45	24.22	58.14	2.82	5.90	42.83	9.41
Marrow	105	1.38	7.65	4.70	22.86	63.41	2.15	7.46	52.51	3.44
Telephone	74	2.90	9.40	6.14	24.38	57.18	3.57	16.29	33.84	7.05

The fiber shows a general decrease from 11.43 per cent in the petits pois extra fins to 7.65 per cent in the marrowfats. The ash decreases from 6.98 per cent to 4.70 per cent in the same classes. The variations in protein appear to be independent of the class of peas. Sugar varies from 5.90 per cent to 17.27 per cent, and is generally higher in the smaller peas. The opposite is true of starch, which is 29.09 per cent in the extra sifted and 52.51 per cent in the marrowfats. The pea ash is very uniform, but the smaller varieties generally carry more sodium chlorid.

ADDITIONS TO CANNED PEAS AND THE USE OF SOAKED PEAS.

There are two practices quite prevalent in the canning of peas—the addition of sugar or glucose to give character to otherwise insipid peas and the use of soaked peas.

[1] U. S. Dept. Agr., Bureau of Chemistry Cir. 54.

Sugars.

The sugar in the liquor ranged from none at all to 5.21 per cent; average, 2.44 per cent, equivalent to 37 per cent of the solids. Fifty-six samples contained glucose which in the liquor ranged from 0.27 to 1.30 per cent. The total reducing sugars in the drained peas ranged from 0.34 per cent to 5.18 per cent; average, 2.26 per cent, or from 1.37 to 28.71 per cent; average, 18.71 per cent in the water-free material. It is very probable that the small amounts of undetermined carbohydrates, from 0.09 to 3.42 per cent, consist chiefly of galactan.

In 18 samples sugar was declared on the label, in 8 "sugar" was used in the brand name, in 22 "sweet" was similarly used, and in 63 no sugar was declared nor was there any claim made of superior sweetness. The sugar content of these four classes of samples was as follows:

Sugar content (water-free basis).

Label.	Maximum.	Minimum.	Average.
Added sugar declared (18)	28.71	7.65	14.02
Sugar in brand name (8)	24.00	8.18	17.06
Sweet in brand name (22)	29.05	6.21	17.77
No reference to sugar or sweetness (63)	24.49	1.37	8.43

While the amount of sugars natural to peas is somewhat in doubt, in those samples in which sugar was declared or indicated the minimum amount in the dry matter is 7.65 per cent. It is not unreasonable to suspect samples showing more than this minimum of containing added sugar. In the 63 samples in which no reference to sugar was made, 27 showed from 1.37 to 7.79 per cent in the dry matter, 7 from 8.06 to 11.46 per cent, 18 from 12.27 to 15.42 per cent, and 11 from 16.21 to 24.49 per cent. The last two classes, numbering 29 samples, certainly contain sugars in amounts exceeding the quantity naturally found in peas. These samples also show excessive amounts of sugar in the pea liquor.

Soaked peas.

In detecting soaked peas the physical appearance of the sample is of some value. Soaked peas are generally more or less broken, the cotyledons well developed, especially in the mature peas, and the liquor more liable to be thick and starchy. Maturity, however, is not an infallible guide, because old and well-developed peas are frequently packed in the fresh condition; nor can cloudiness of liquor always be depended upon, for mature fresh peas, overprocessed, or packed with too little liquor, will give a liquor very similar to that of soaked peas. Dubois has shown that "it is not hard to distinguish the fresh and more succulent grades from the soaked material, the chief difficulty arising in differentiating between the soaked goods and the more matured peas put up in the usual way."

In the analyses here reported the starch (all water-soluble carbohydrates having been removed before hydrolysis) was found to range from 2.04 to 15.65 per cent (average 7.64 per cent) in the original drained peas, or from 21.38 to 59.78 per cent (average 39.92 per cent) on the water-free basis. In the following summary the samples are grouped according to starch content in the original material, showing the variations in water content of the drained peas, the solids of the liquor, and the starch of the drained peas in the dry material:

Comparative data on samples grouped according to starch content.

Per cent of starch.	Number.	Average starch.	Water in drained peas, original material.			Solids in liquor, original material.			Starch in drained peas, water-free.		
			Maximum.	Minimum.	Average.	Maximum.	Minimum.	Average.	Maximum.	Minimum.	Average.
Under 4	13	3.40	90.46	82.83	86.78	8.92	4.69	6.17	31.66	21.38	25.72
Under 5	17	4.43	86.66	82.17	84.29	8.59	5.29	7.09	34.47	22.77	28.20
Under 6	14	5.54	86.10	81.11	82.49	8.82	5.15	7.16	37.63	29.17	31.64
Under 7	14	6.64	83.55	78.87	81.00	8.54	4.16	6.41	41.28	30.63	34.95
Under 8	9	7.56	83.66	77.04	80.71	8.87	3.88	5.98	46.14	32.84	39.19
Under 9	10	8.61	81.75	76.90	79.44	7.79	3.73	6.06	47.21	36.32	41.88
Under 10	7	9.59	80.66	76.22	78.25	7.36	3.77	6.24	50.18	39.07	44.09
Under 11	6	10.56	80.24	78.19	78.77	7.80	4.88	6.41	55.41	46.18	49.74
Under 12	6	11.58	77.97	75.94	76.90	10.68	6.95	8.29	52.05	48.76	50.13
Over 12	15	13.37	76.63	73.82	74.92	8.04	4.89	6.81	59.78	48.52	53.31

On the average there is quite a close relation between the amount of water and starch in the drained peas and the amount of starch in the liquor. The average water content steadily decreases as the starch increases. Unfortunately, confirming Dubois's experience, there is an overlapping of results in individual analyses, and the distinction between the soaked and the fresh peas is at times far from clear.

Grouping the samples according to starch content, 30 contained from 21 to 30 per cent, 38 from 31 to 40 per cent, 30 from 41 to 50 per cent, and 13 over 50 per cent in the dry material. Judging from our present information a sample showing 45 per cent or more of starch in the dry matter is certainly open to suspicion as to consisting either of very mature or soaked peas; there are 35 such among my samples. In 3 of these the liquor was slightly cloudy, in 11 cloudy, in 16 thick, and in 5 very thick; in 9 the consistency of the peas was good, in 23 they were hard, and in 3 soft; the cotyledons were prominent in 22, not prominent in 11, variable in 2. Accepting as characteristics of soaked peas a thick or very thick liquor, peas of hard consistency, cotyledons prominent, and a starch content of over 45 per cent, 16 of my samples are in harmony with these requirements. These samples likewise show a low water content from 72.83 to 78.51, average 75.74 per cent, as compared with the general average of 80.86 per cent, and the maximum of 90.46 per cent.

Metals.

Copper was found in 14 samples, in 12 of which it was declared on the label. The amounts present ranged from 8 to 67 mg per kilo of drained peas; in 3 the large quantities of 45, 58, and 67 mg were found.

Tin was found in weighable quantities in 88 samples, in quantities ranging from 2 to 395 mg per kilo. Thirteen samples contained both copper and tin.

Ketchup.

GENERAL ANALYSES.

Seventy-four samples of ketchup were analyzed, representing the product of 56 manufacturers or jobbers. In a material of such complex and variable nature as ketchup wide variations in composition are to be expected. It would seem, however, that certain of the chemical characteristics of the tomato should still persist in the manufactured product.

As a starting point, a number of fresh tomatoes were carefully separated into pulp, juice, skin, and seeds, and the separate portions analyzed, with the following results:

Analysis of fresh tomatoes.

Parts of tomato.	Original substance.	Dry matter.	Per cent of tomato.
	Grams.	*Grams.*	
Whole tomato	1,455	70.75	.....
Pulp and juice	1,237	51.00	85.02
Seeds	75	9.75	5.15
Skins	143	10.00	9.83

Determinations.	In original fruit.				In water-free material.			
	Whole fruit.	Pulp and juice.	Seeds.	Skins.	Whole fruit.	Pulp and juice.	Seeds.	Skins.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Water	95.63	96.38	87.45	93.54	.....	.....	.....	.....
Ether extract	.27	.09	3.38	.11	6.18	2.49	26.93	1.70
Fiber	.46	.22	1.93	1.75	10.53	6.08	15.38	27.09
Protein (N×6.25)	.85	.65	3.89	.97	19.45	17.96	31.00	15.02
Ash	.42	.41	.44	.48	9.61	11.33	3.51	7.43
Nitrogen-free extract	2.37	2.25	2.91	3.15	54.23	62.14	23.18	48.76
Water-soluble solids	2.93	2.98	2.25	2.84	67.05	82.32	17.93	43.96
Ratio insoluble to total solids (1:—)	3.0	5.7	1.2	1.8	.....	.....	.....	.....

Each of the parts of the fruit appears to have rather marked characteristics. In the pulp and juice the insoluble solids are low, the ash high, the fiber low, and the protein medium. In the seeds the insoluble solids are very high, the ash low, the fiber medium, and the protein high. In the skins the insoluble solids are high, the ash medium, the fiber very high, and the protein low. The significance of these data in the analysis of ketchups will be referred to later.

The 74 samples were divided into 3 groups—those which contained no sodium benzoate, those which contained benzoate not in excess of the amount claimed, and those whose benzoate exceeded the claimed amount. This classification seems to be the simplest, and at least offers a definite starting point. Of the 8 samples claiming no benzoate on the label only one contained the preservative, 0.25 per cent; 1 claiming 0.03 contained 0.10 per cent; 3 which claimed benzoate with no statement of quantity contained 0.13, 0.21, and 0.23 per cent; 62 claimed the usual 0.10 per cent, 45 exceeding this amount and containing from 0.11 to 0.38 per cent. To summarize, 7 contained no benzoate, 18 from 0.04 to 0.10 per cent, 30 from 0.11 to 0.20 per cent, 14 from 0.21 to 0.30 per cent, and 5 over 0.30 per cent. Of the 63 samples claiming definite amounts 46, or 73 per cent, exceeded that amount, and 5 contained over three times the amount claimed. Below will be found the average analyses of the nonbenzoated and benzoated samples.

Average analyses of ketchups.

Determinations.	Containing no benzoate.	Containing benzoate.	All (74) samples.
Original substance:	*Per cent.*	*Per cent.*	*Per cent.*
Water	76.91	84.20	83.78
Insoluble solids	2.00	2.35	2.32
Ash	3.48	3.38	3.39
Ash (sodium chlorid)	.94	.98	.98
Fiber	.42	.50	.49
Protein	1.76	1.50	1.53
Acetic acid	1.35	1.08	1.11
Water-free basis:			
Insoluble solids	9.09	15.90	15.26
Ash	16.06	22.53	21.91
Ash (sodium chlorid)	4.26	6.60	6.38
Fiber	1.96	3.49	3.35
Protein	8.07	9.69	9.53
Water-salt-free basis:			
Insoluble solids	10.41	19.24	18.40
Ash	4.87	7.97	7.68
Fiber	2.24	4.25	4.06
Protein	9.26	11.63	11.41

The samples showed very wide variations in composition. In the benzoated samples the water ranged from 71.74 to 92.73 per cent, insoluble solids from 1.23 to 6.07, ash from 1.61 to 6.89, sodium chlorid from 0.71 to 5.17, fiber from 0.32 to 0.77, protein from 0.81 to 3.06, and acidity from 0.54 to 1.68. The nonbenzoated samples showed more uniformity, but there were wide variations in water content and acidity.

Summary of extremes in all samples. (Original substance.)

Solids	7.27–32.49
Insoluble solids	1.23– 6.07
Ash	1.61– 6.89
Sodium chlorid	.71– 5.17
Fiber	.32– .77
Protein	.81– 3.06
Acetic acid	.54– 1.98
Sodium benzoate	.00– .38

ACIDITY.

The acidity of the nonbenzoated samples ranged from 0.85 to 1.98, that of the benzoated from 0.54 to 1.68. It is frequently claimed that the manufacturers of nonbenzoated ketchups employ acetic acid extracts of spices and secure a preservative effect by the excessive acidity. At first glance our acidity figures seem to lend some weight to this contention, for the two nonbenzoated samples showing the highest acidities, 1.83 and 1.98 per cent, are 0.15 and 0.30 per cent higher than the highest benzoated samples. It is most unfair, however, to consider acidity apart from its relation to solids. A ketchup might show a low acidity and yet be so low in solids that a very large quantity would be necessary to secure the desired condimental effect, while on the other hand, a ketchup high in acidity might be so high in solids that only a small quantity would be needed to secure the same effect, and the acidity of the actual amount of ketchup used would be lower than in the low-solids ketchup. Such is the case in the two samples just referred to. In the nonbenzoated ketchups the ratio of acidity to solids ranged from 12.7 to 24.8, average, 17.1, while in the benzoated samples the ratio ranged from 5.4 to 29.8, average, 14.7. The two nonbenzoated samples with high acidities showed the high ratios of 12.7 and 16.4. In 20 of the benzoated samples the ratio of acidity to solids was lower than in the lowest of the nonbenzoated samples.

TOTAL SOLIDS.

The total solids ranged from 7.27 to 32.49 per cent, average, 16.22 per cent. In 6 the solids were over 24 per cent, in 9 from 20 to 24, in 31 from 15 to 20, in 20 from 10 to 15, and in 8 under 10 per cent. The amount of solids considered by itself is not a safe criterion, for this may be due in great part to added salt, sugar, glucose, or cereal, and may have but a slight relation to true tomato solids.

SALT.

In the original substance the salt ranged from 0.71 to 5.17 per cent, or from 4.69 to 28.88, water-free. In 2 samples the salt made up less than 5 per cent of the solids, in 11 from 5 to 10 per cent, in 26 from 10 to 15 per cent, in 17 from 15 to 20 per cent, in 13 from 20 to 25 per cent, and in 5 over 25 per cent. The 5 samples showing over 25 per cent of salt in the dry matter are particularly interesting, as the following tabulation shows.

Results on five samples high in salt.

Total solids.	Per cent of salt in solids.
15.43	25.41
7.45	26.71
8.47	27.04
8.14	27.15
7.27	28.88

That is, some of the samples showing the lowest total solids, contained over 25 per cent of these solids as common salt.

WATER-SALT-FREE BASIS.

Inasmuch as the quantity of spice used is relatively small compared with that of tomato pulp, the solids obtained by calculating to a dry salt-free basis in a pure tomato ketchup should consist almost entirely of tomato solids and sugar. As the sugar contains practically no ash, fiber, protein, or insoluble solids, the percentages obtained for these ingredients by this method of calculation can be fairly attributed to the tomato, provided, of course, we are dealing with a pure tomato ketchup. Accordingly, all the analyses were recalculated to this basis.

INSOLUBLE SOLIDS.

These ranged from 1.23 to 6.07 in original substance, from 6.43 to 33.15, dry basis, and from 7.10 to 45.24 per cent water-salt-free basis. A large proportion of tomato pulp solids is soluble in water (over 80 per cent), while in skins and seeds the solubility is only about 44 and 18 per cent, respectively. A high proportion of insoluble matter, therefore, should arouse suspicion as to the use of skins or seeds, or the addition of some insoluble matter like starch. In one of our samples where wheat flour was declared in the label, 36 per cent of the salt-free solids were insoluble in water; in another, where cereals were declared, over 45 per cent were insoluble.

In 6 samples the ratio of insoluble to total solids was over 10, in 19 from 7 to 10, in 37 from 4 to 7, and in 12 less than 4. In 8 of these 12 the label declared the presence of other materials than tomato pulp. These are given in some detail in the following tabulation:

Insoluble solids in ketchups declaring foreign materials.

Foreign substance declared.	Per cent insoluble salt-free solids.	Ratio of insoluble to total salt-free solids.	Foreign substance declared.	Per cent insoluble salt-free solids.	Ratio of insoluble to total salt-free solids.
Tomato trimmings	19.82	1 : 5.0	Apples	31.47	1 : 3.2
Cereals	35.79	2.8	Do	32.72	3.2
Do	45.24	2.2	Do	39.32	2.5
Apples	23.33	4.3	Average (6 high-grade ketchups)	8.88	11.4
Do	28.32	3.5			

ASH.

The ash determinations ranged from 1.69 to 6.89 in original substance, and from 8.22 to 40.08 per cent, water-free. The salt-free ash ranged from 0.55 to 1.78, original, from 2.86 to 15.74, water-free, and from 3.16 to 20.80 per cent, water-salt-free.

In pure tomato pulp and juice it was found that the ash made up 11 per cent of the water-free substance. Because of the use of sugar, which contains no ash, and other materials relatively low in ash compared with tomato pulp, the salt-free ash should be much lower in ketchup than that in the original pulp. While it is difficult to set a maximum limit, the ketchups themselves show what should be expected in a high-grade product. For instance, the salt-free ash was under 5 per cent in 9, from 5 to 8 in 40, from 8 to 10 in 13, and over 10 in 12 samples. The 27 samples containing about 6 per cent of salt-free ash or less, include what are recognized as the highest grade brands, that is, high grade from the standpoint of quality of materials used and entirely independent of whether or not benzoate is present. It is a striking fact, however, that the nonbenzoated samples contained only from 3.16 to 6.21 per cent, while the benzoated contained from 3.71 to 20.80 per cent, only 21 of 67 samples containing less than 6 per cent. Adopting the best trade practice as a basis of judgment, samples containing much over 6 per cent of salt-free ash in the dry salt-free material must be considered with suspicion, and those containing over 10 per cent as not pure. That is, 12 of the samples must be considered as more than suspicious. These in the dry salt-free substance contained from 10.04 to 20.80 per cent of salt-free ash, from 16.44 to 45.24 per cent of insoluble solids, from 4.33 to 10.88 per cent of fiber, and from 14.13 to 24.63 per cent of protein, all of these data indicating inferiority.

FIBER.

The fiber ranged from 0.32 to 0.77 per cent original, from 1.29 to 8.26 water-free, and from 1.42 to 10.88 water-salt-free. High fiber is characteristic of tomato seeds and skins, especially the latter. In the dry salt-free material 17 samples contained less than 2.50 per cent, 29 from 2.50 to 4 per cent, 16 from 4 to 5.50 per cent, and 12 over 5.50 per cent. The high percentages of fiber were, as a rule, associated with high insoluble solids and high salt-free ash.

PROTEIN.

This ranged from 0.81 to 3.06 per cent original, from 4.88 to 18.75 per cent water-free, and from 5.38 to 24.63 per cent water-salt-free. High protein, about 31 per cent, is the most marked characteristic of tomato seeds. In the dry salt-free substance 18 samples contained less than 9 per cent, 27 from 9 to 12 per cent, 19 from 12 to 15 per cent, and 10 over 15 per cent. Those containing the greatest amounts of protein as a rule were high in salt-free ash, insoluble solids, and fiber.

SUGAR, GLUCOSE, AND STARCH.

All of the samples were polarized before and after inversion. The presence of acetic acid rendered the exact determination of sucrose and invert sugar difficult, and the percentages given are only approximate. The total sugars ranged from none to 24 per cent. The tomato itself contains much sugar (according to König, 50 per cent of the dry matter) and the presence of sugar in ketchup is to be expected; its absence would indicate that little if any tomato pulp and juice had been employed unless fermented stock was used. The presence of glucose, however, should be declared. Only two brands made such a declaration, and these contained 13.75 and 13.36 per cent of glucose, making up nearly 50 per cent of the solids. Twelve other samples contained from 0.39 to 5.01 per cent.

Starch was not determined quantitatively, but all the samples were examined under the microscope for starch. Pepper or paprika starch was observed in many samples, and its presence is entirely proper. Cereals, however, add nothing of condimental value and serve simply as makeweight, or as a means of giving body to an otherwise thin ketchup. Nine samples contain cereal starch, in only two of which it was declared. The figures given for "undetermined" chiefly represent starch, and in certain samples this is very high. For instance, two samples showed 10.15 and 13.07 per cent.

SACCHARIN.

In five samples saccharin was declared on the label, and these are all among the lowest grades of ketchup. Two others gave zero polarization readings before and after inversion, and this would suggest the presence of saccharin, although the pungency of the spices used prevented its certain identification.

COLOR.

Nine samples contained artificial color and on seven it was declared.

SUGGESTED LIMITS OF COMPOSITION.

A careful study of our tabulated analyses showed that no safe conclusions as to quality could be drawn from the ratios above referred to, except that of insoluble to total salt-free solids. This ranged from 2.2 to 14.1 in the 74 samples, or, in other words, the insoluble solids made up from 7.10 to 45.24 per cent of the salt-free solids.

The data on two groups of samples have been tabulated, the first consisting of 16 brands generally recognized as high grade, the second consisting of 13 brands, which either condemn themselves by the information given on their labels or are shown to be low grade by analysis. The following table shows the maximum, minimum, and average of the various ingredients in the two groups:

Average composition and extremes for high-grade and low-grade ketchups.

Determination.	High grade (16 samples).			Low grade (13 samples).		
	Maximum.	Minimum.	Average.	Maximum.	Minimum.	Average.
In original substance:						
Total solids	32.49	14.22	20.56	16.42	7.27	9.55
Sodium benzoate	.20	.00	.08	.30	.07	.18
Sodium chlorid in total solids	18.92	4.90	12.46	28.88	15.63	23.84
In salt-free dry substance:						
Insoluble solids	14.24	7.10	11.22	45.24	21.34	30.04
Ash	6.97	3.16	5.38	16.19	7.78	12.73
Fiber	4.10	1.42	2.56	10.88	4.89	7.72
Protein	12.00	5.38	9.06	24.63	12.00	17.33
Ratio insoluble to total solids (1 : —)	14.1	7.0	8.9	4.7	2.2	3.3

In the samples classed as high grade the maximum of insoluble solids is 14.24; ash, 6.97; fiber, 4.10; protein, 12 per cent; and the lowest ratio of insoluble to total solids is 1:7. In those classed as low grade these maxima are exceeded in every case, and the highest ratio is 1:4.7. It is interesting to note that all but one of the seven samples found to contain no benzoate are included in the high-grade class. The low grade brands on the average contained more than twice as much benzoate as the high-grade. Likewise the proportion of salt to total solids is on the average nearly twice as high in the low grade. The 45 other brands not included in the above groups all possess some of the characteristics of one or the other group, but none shows all the characteristics of either.

As a tentative standard it is suggested that pure tomato ketchup should contain in the salt-free dry substance not more than 15 per cent of insoluble solids, not more than 7 per cent of ash, not more than 4 per cent of fiber, and not more than 12 per cent of protein; the ratio of insoluble to total salt-free solids should not be less than 1:7.

OCCURRENCE AND ESTIMATION OF TIN IN FOOD PRODUCTS.

By Bernard H. Smith and George M. Bartlett.

It has long been recognized that canned food products almost invariably contain appreciable quantities of tin compounds. In 1878 Menke [1] called attention to the presence of tin [2] in canned pineapple, apples, and lobster. In 1880 Hehner [3] reported an investigation of canned foods, finding tin present in all samples examined in quantities varying from 8 to 45 mg (calculated as metallic tin) per pound. The vegetable foods examined were asparagus, peas, tomatoes, peaches, pineapples, and cherries. The animal foods studied included beef of different kinds, tripe, oysters, sardines in oil, salmon, lobster, shrimp, rabbit, chicken, mutton, and condensed milk. He also conducted experiments with guinea pigs to test the toxic properties of stannous and stannic hydroxids, and as a result of this work he came to the conclusion that tin in the form of stannic hydroxid has but little physiological effect, but that stannous hydroxid is a powerful irritant poison, and that canned goods containing appreciable quantities of tin in solution "can not but be more or less injurious."

In 1883 Ungar and Bodländer [4] showed that certain canned goods contained marked amounts of tin, and as a result of experimental research they came to the conclusion that insoluble tin compounds are dissolved and absorbed during digestion. Later a number of investigations of tin plate and the tin content of canned foods are reported, among which are those of the United States Department of Agriculture, Bureau of Chemistry, in 1892, and the Massachusetts State Board of Health from 1894 to 1899. An interesting case is described by Günther,[5] who reports that he was poisoned by the tin of canned herrings in wine sauce. He also states that in examining canned fish he found three or four times as much tin in the solid portion as in the sauce. Wirthle [6] corroborated this by showing that canned meats contained much more tin in the solid portion than in the liquor.

In the routine inspection of food products the corrosion of the containers of some varieties of canned goods was often observed, particularly of certain fish products, and a systematic examination of such of these as are imported through the port of Boston was begun early in the year. Approximately 25 per cent of the samples examined (which were chosen because the tins of the shipment were corroded or discolored) contained more than 300 mg of tin per kilo, which amount is slightly more than is allowed as the maximum tin content of food products in England. The

[1] Chem. News, 1878, 38: 971.
[2] In compounds.
[3] Analyst, 1880, 5: 218.
[4] Zts. Hyg., 1887, 2: 241; Abst. Chem. Centrbl., 1887, p. 644.
[5] Zts. Nahr. Genussm., 1899, 2: 915.
[6] Chem. Ztg., 1900, 24: 263.

following kinds of fish were found to be most affected: Fish in acid, such as soused mackerel and pickled fish; fish in the various sauces, such as in wine, mustard, or tomato sauce; fish in bouillon; spiced anchovies; smoked fish, such as kippered herring; also canned cod and lobster contained much tin when the container was unprotected; to a less extent sardines in oil, tunny fish in oil, and clams were found at fault.

Foreign packers in general use a better grade of tin plate than that in use in this country, and because the worst instances of corrosion are found with inferior plate our attention was directed to similar domestic products. The same class of fish products of domestic origin were found to contain excessive quantities of tin, especially sardines in "mustard sauce." Goods which have been put up a considerable time invariably show greater amounts of tin than those of the same character when freshly packed, and as a sample of sardines in mustard examined, which was said to have been packed within a month, contained a large amount of tin, arrangements were made early in the summer to have some processed under prevailing factory conditions and by the usual commercial methods, under the supervision of the writers, for the purpose of ascertaining how rapidly the container was corroded. The mustard sauce in which the fish were packed was composed of ground mustard seed, vinegar, salt, cayenne pepper, and turmeric, and the processing was continued for two hours.

The lot was shipped promptly from Eastport to Boston, where the first examination was made without delay, subsequent analyses being made at intervals of approximately two weeks; the results obtained are given in the following table; figure 3 shows the data in graphic form:

Tin determinations in sardines in mustard put up under known conditions.

Dates of analysis:	Mg of tin per kilo.
June 14	257
June 28	420
July 15	619
July 27	780
August 13	846
August 29	935
September 16	Lost.
September 28	859
October 17	875

All determinations were made on a composite sample of the contents of three tins. There is considerable individual variation in the tin content of containers of this kind when packed under commercial conditions, primarily owing to differences and flaws in the tin plate; the irregular result of August 29, which is abnormally high, when compared with the other results, is doubtless due to this cause. The table shows that under the present methods of packing the tins are corroded with startling rapidity and that this food is contaminated with nearly 0.1 per cent of tin in a very few months.

It is our belief that the considerable amount of salt which is present with the acetic acid causes the formation of small amounts of hydrochloric acid, which would readily attack the tin. This tendency toward solution would be augmented by any electrolytic action that might take place. In our work with canned fish products it was invariably noticed that the corrosion of the container is greatest where the fish comes in contact with the tin. The data obtained also corroborated that of other workers with flesh products who have found more tin in the solid than in the liquid portion, and we are of the opinion that the larger part of the tin is ultimately combined with the proteins, which might be expected from the manner in which tin salts precipitate

certain proteins.[1] Sardines in oil, when the tin is well filled with oil, do not show large quantities of tin.

The literature as to the toxicity of tin is limited, but most of those who have investigated the subject believe that tin salts, especially stannous salts, are injurious. The conditions existing in a hermetically sealed can of a foodstuff, as has been pointed out by Hehner, are conducive to the formation of stannous compounds, and when the wide and growing use of canned products is considered, the problem becomes a serious one.

The principal packers of canned lobster, shrimp, and codfish have used a parchment paper lining for some time with satisfactory results. This is impracticable in the case of sardines in mustard sauce, but lacquered tins have been tried in an experimental way by a number of packers successfully. Samples of these goods which had been packed for from one to two years were examined and contained only from 100 to 300 mg of tin per kilo, and when the process has passed beyond the experimental stage

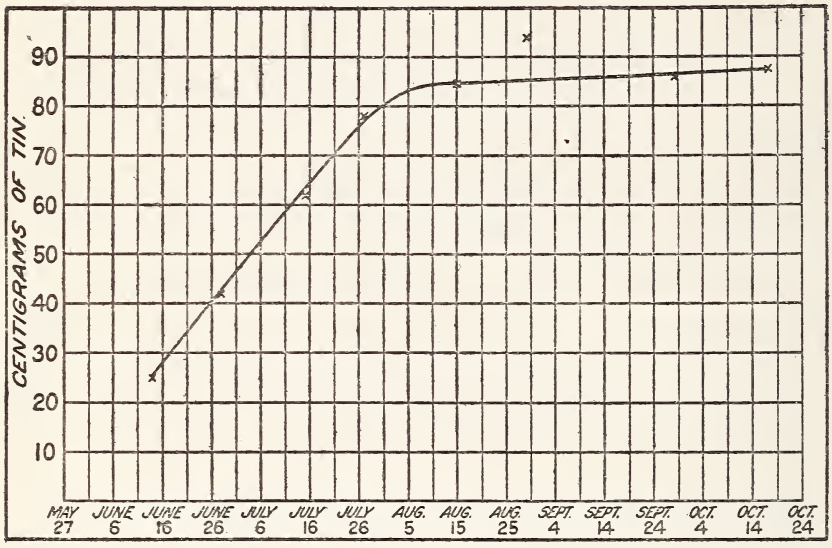

FIG. 3.—Curve showing increase of tin content of sardines in mustard sauce.

much better results should be obtained. The cost of lacquering is about one-tenth of a cent each for the usual sized sardine tin; the use of lacquered tins for many food products is becoming quite general in several European countries. A cement lined tin has also been proposed.

The official methods as outlined in Bulletin 107, Revised, Bureau of Chemistry, for the determination of tin can not be relied upon to give the total amount of tin in a food product. The estimation is one of some difficulty, but the following method has proved satisfactory to the writers:

Weigh 50 grams of fish or 100 grams of vegetables in a porcelain dish and, preferably, dry overnight. Heat from 75 to 100 cc of sulphuric acid (1.84 sp. gr.) in a Kjeldahl flask until the acid fumes are visible. Add gradually small portions of the food product, the acid being heated between additions until no further frothing occurs. The first operation in this procedure is the most difficult, but if care is taken and the sample is added cautiously, but little difficulty will be experienced. When all the sample has been added to the flask, allow to cool, the sample being completely charred. Then add gradually 25 cc of nitric acid (1.42

[1] Zts. anal. Chem., 1898, 37: 73.

sp. gr.): Red fumes are given off for a few moments and the flask becomes warm. After allowing to cool again, add 25 cc of nitric acid and heat gently until all nitric fumes have been driven off. This procedure should dissolve the charred contents, making a perfectly homogeneous solution. Boil this solution about three-quarters of an hour, then add from 10 to 15 grams of potassium sulphate and continue boiling, the solution becoming discolorized in from three to five hours after the addition of the potassium sulphate. If the potassium sulphate is added too soon, frothing, dangerous to the accuracy of the determination, is liable to occur. Now wash the digest from the flask into an 800 cc beaker, dilute to 600 cc volume, and bring to a boil. Almost all of the tin separates as stannic oxid, more or less hydrated, but the flask retains some stannic oxid adhering to the sides, which can not be removed by washing with water. The contents of the beaker having been boiled, filter, thus separating the hydrated stannous oxid from all other compounds. Place the filter in the flask, to which 20 cc of saturated sodium hydroxid and an equal volume of water have been added. The contents are boiled for several minutes, after which the sodium stannate formed may be washed into a beaker. Acidify with hydrochloric acid and precipitate with hydrogen sulphid as directed in Bulletin 107, Revised, page 69.

The solution of the stannic oxid in caustic soda is generally necessary, as it may be but little hydrated and will not be changed to stannic sulphid by merely passing hydrogen sulphid through the oxid suspended in water. When but slightly hydrated it usually has a granular appearance, and even ammonium sulphid under pressure will not dissolve the granular stannic oxid quantitatively. Complete conversion to stannic sulphid may, however, be obtained by boiling with sodium hydroxid as described, acidifying, and precipitating with hydrogen sulphid. If, on the other hand, the precipitate from the water digest is flocculent, it may be dissolved by ammonium sulphid in a pressure bottle.

Small amounts of tin may occur in the filtrate from the water digest. This evidently is stannous sulphate, since stannic salts are precipitated as hydrated stannic oxid by boiling with alkali sulphates or ammonium nitrate. ($SnCl_4+4Na_2SO_4+3H_2O=H_2SnO_3+4NaHSO_4+4NaCl$, Löwenthal, J. prakt. Chem., 1852, **56**: 366).

The filtrate should always be tested for tin with hydrogen sulphid. The tin sulphids thus obtained can be dissolved readily with ammonium sulphid and reprecipitated as directed in Bulletin 107, Revised. We have preferred to dissolve the tin sulphid in a pressure bottle. The ammonium sulpho-stannate may then be treated with glacial acetic acid, whereby the tin is obtained as stannic sulphid. This is filtered, washed, ignited, and weighed as stannic oxid.

CONSTANTS OF THE ETHER EXTRACT OF THE CASHEW NUT.

By Bernard H. Smith and Edmund Clark.

Introductory.

The cashew nut, the seed of *Anacardium occidentale* L., is annually being imported into the United States in increasing quantities. This is partly because the nut is becoming more widely known, but it is principally because its bland flavor and low price—10 to 18 cents per pound for the roasted meats—admit of its substitution for the almond in almond pastes, chopped nuts, and similar preparations used by bakers and confectioners. The name refers to the heart-shaped seed, which is borne on a fleshy receptacle varying from the size of a cherry to that of a pear, the seed usually being about 1 inch in length. It contains from 45 to 50 per cent of oil, and considerable starch.

The constants of the filtered and dried ether extract are given in the following tabulation:

Ether extract (not on moisture-free basis) per cent	46.17
Mixed fatty acids (gravimetric) per cent	94.37
Liquid acids (obtained by difference) per cent	70.84
Solid acids (gravimetric) per cent	23.53

CONSTANTS OF ETHER EXTRACT.

Refractive index at 25° C.	1.4673
Specific gravity at $\frac{15°\ C.}{15°\ C.}$	0.9166
Saponification value	192
Iodin value (Hanus)	83 83.4
Hehner value	94.4
Soluble acids	None.
Acetyl value (Lewkowitsch method)	8.98
Saponification value of acetylated product	197.3

CONSTANTS OF MIXED FATTY ACIDS.

Refractive index at 60° C.	1.4459
Specific gravity at 15° C. (obtained by alcohol)	0.8986
Melting point (capillary tube)	33° to 34° C.
Neutralization value	192.9
Mean molecular weight (calculated)	290.9
Iodin value (Hanus)	83.16

CONSTANTS OF LIQUID ACIDS.

Neutralization value	179.5
Mean molecular weight (calculated)	312.5
Iodin value (Hanus)	104.0

CONSTANTS OF SOLID ACIDS.

Neutralization value	194.7
Mean molecular weight (calculated)	288.1
Arachidic acid	None.

REPORT ON WATER IN FOODS.

By P. F. Trowbridge, *Associate Referee.*

No samples for cooperative work were sent out, but several chemists were asked to investigate the influence of the methods of making moisture estimations upon subsequent operations, especially on the determination of fat (ether-soluble substances).

In the Missouri laboratory the vacuum method without heat [1] has been used for several years for making moisture determinations in all of our meat investigations and this year it is being used in determining the moisture in nearly all substances which require a determination of the fat (ether-soluble substances). For the purpose of this special report three samples of ice cream were chosen. By the official method using heat, 11, 5, and 10 dryings, respectively, were necessary to give constant weight or until the loss in weight between two successive dryings did not exceed 5 mg. Triplicate determinations on each gave the moisture per cent as shown by the following table, which also gives the subsequent fat (ether-soluble) determinations. The latter are far from satisfactory. The dry residue was considerably darkened.

These three samples of ice cream were also dried in vacuum without any heat, and showed constant weight on the second weighing. Before the first weighing the tubes were transferred to desiccators containing fresh acid. A comparison of the results in Table 1 will show that the vacuum method without heat gives as high or higher results for moisture and that the subsequent ether-soluble estimation is much more satisfactory.

[1] U. S. Dept. Agr., Bureau of Chemistry Bul. 122, p. 219.

TABLE 1.—*Moisture and fat (ether-soluble) in ice cream.*

Sample number and method.	Net weight of sample.	Weight of container and sample.	Weights on consecutive dryings.											Total loss in drying.	Moisture.	Fat (ether-soluble).
			First.	Second.	Third.	Fourth.	Fifth.	Sixth.	Seventh.	Eighth.	Ninth.	Tenth.	Eleventh.			
A. Official method:	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Per cent.*	*Per cent.*
5a	17. 6958	63. 2177	51. 6885	50. 8660	50. 6017	50. 5000	50. 4460	50. 3806	50. 3626	50. 3306	50. 2750	50. 2700	50. 2668	12. 9509	73. 18	5. 437
5b	16. 7739	62. 8416	51. 6450	50. 9350	50. 7195	50. 6380	50. 5940	50. 5433	50. 5267	50. 4890	50. 4502	50. 4432	50. 4407	12. 4009	73. 93	4. 788
5c	20. 8987	67. 0664	53. 8680	52. 5947	52. 1545	51. 9180	51. 8350	51. 7261	51. 6883	51. 6300	51. 5788	51. 5662	51. 5631	15. 5033	74. 18	4. 247
Average															73. 76	4. 824
6a	11. 9833	58. 0356	49. 4568	49. 3419	49. 3113	49. 2945	49. 2910							8. 7446	72. 97	2. 667
6b	12. 4732	58. 6281	49. 7275	49. 5927	49. 5311	49. 5100	49. 5080							9. 1201	73. 12	2. 521
6c	13. 1335	60. 8214	42. 4188	41. 3238	41. 2500	41. 2256	41. 2178							9. 6036	73. 12	2. 292
Average															73. 07	2. 493
7a	12. 4214	50. 3856	41. 8397	41. 3233	41. 2230	41. 1700	41. 1518	41. 1216	41. 1167	41. 1030	41. 0862	41. 0831		9. 3025	74. 89	1. 922
7b	11. 8560	50. 4621	42. 2946	41. 8576	41. 7415	41. 6951	41. 6780	41. 6464	41. 6370	41. 6166	41. 5948	41. 5905		8. 8716	74. 83	2. 287
7c	11. 4563	50. 3651	42. 6086	42. 0857	41. 9740	41. 9220	41. 9036	41. 8695	41. 8595	41. 8561	41. 8150	41. 8112		8. 5539	74. 67	2. 112
Average															74. 80	2. 107
B. Vacuum method without heat:																
5a	11. 7195	49. 2727	40. 2189	40. 2155										9. 0572	77. 28	4. 332
5b	10. 0883	47. 4233	39. 6359	39. 6355										7. 7878	77. 20	4. 110
Average															77. 24	4. 221
6a	8. 8555	46. 2947	39. 8951	39. 8924										6. 4023	72. 30	3. 072
6b	12. 6280	50. 1776	41. 0414	41. 0380										9. 1396	73. 17	3. 289
Average															72. 74	3. 181
7a	8. 7785	46. 2763	39. 7042	39. 7023										6. 5740	74. 89	3. 877
7b	7. 9240	45. 9484	39. 9350	39. 9325										6. 0159	75. 92	3. 563
Average															75. 41	3. 720

In some cooperative work done at the Missouri experiment station a complete analysis was made of nearly 100 samples of corn meal. In the moisture determinations by the official method 12 of the samples varied by more than 0.3 per cent in the duplicate samples. The moisture determination on these 12 samples was repeated by the vacuum method without heat and in every case satisfactory duplicate results were obtained, the lower of which was much higher than the highest by the official method.

As is seen by the following table, this average increase by the vacuum method without heat in all 12 samples is 1.210 per cent.

TABLE 2.—*Comparison of methods for moisture in corn meal.*

Laboratory number and average.	Moisture.		Laboratory number and average.	Moisture.	
	Official method.	Vacuum method.		Official method.	Vacuum method.
10714	10.985	12.635	10740	12.065	12.870
	10.500	12.725		11.575	12.710
Average	10.743	12.680	Average	11.820	12.790
Gain		1.937	Gain		.970
10720	11.745	12.870	10743	11.380	12.650
	11.290	12.930		12.010	12.675
Average	11.518	12.900	Average	11.695	12.663
Gain		1.382	Gain		.968
10724	11.965	12.855	978	13.430	13.910
	11.260	12.820		12.825	13.985
Average	11.613	12.838	Average	13.128	13.948
Gain		1.225	Gain		.820
10728	10.435	11.270	989	9.595	10.875
	9.695	11.270		8.885	10.640
Average	10.065	11.270	Average	9.240	10.758
Gain		1.205	Gain		1.518
10730	10.440	11.395	10112	8.565	9.275
	9.910	11.515		8.130	9.310
Average	10.175	11.455	Average	8.348	9.293
Gain		1.280	Gain		.945
10734	10.665	11.545	1042	8.405	9.215
	9.990	11.480		7.825	9.190
Average	10.328	11.513	Average	8.115	9.203
Gain		1.185	Gain		1.088

President Withers reported that, with the approval of the executive committee, he had, at the request of the Society for the Promotion of Agricultural Science, appointed a committee to represent the association at a conference called by said society to meet in Washington in November to consider the cooperation of the various agricultural organizations. The personnel of the committee was as follows: H. W. Wiley, chairman, and W. D. Bigelow, of Washington, D. C., and F. W. Woll, of Madison, Wis. The delegates were not given power to bind the association in any way, but were instructed to act solely in an advisory capacity and report the result of the conference to the association for action. The association confirmed the action of the executive committee, and later C. B. Williams, of

Raleigh, N. C., was appointed to act as an alternate for Mr. Woll, who could not be present. The meeting was called for the Tuesday following the meeting of the association, November 15.

REPORT OF COMMITTEE ON NOMINATIONS.

Mr. Frear, chairman of the committee, presented the following report:

The committee on nomination of officers for the ensuing association year respectfully reports the following list of nominations: For president, F. W. Woll, of Wisconsin; for vice president, H. J. Patterson, of Maryland; for secretary, H. W. Wiley, of Washington, D. C.; for additional members of the executive committee, Herman C. Lythgoe, of Massachusetts, and P. F. Trowbridge, of Missouri.

The secretary was instructed to cast the unanimous ballot of the association for these officers.

The following memorial to Albert E. Leach, who died on August 22, 1910, was presented by Mr. Lythgoe, and the resolutions were adopted by a rising vote.

MEMORIAL TO ALBERT E. LEACH.

Whereas Albert Ernest Leach, a man of the highest attainments and loftiest ideals, who for years has been prominently identified with the work of this association, has been separated from us by death; and

Whereas by his untimely death the scientific world, the cause of pure food, and this association have lost an able and devoted worker and the members of this association a dear friend; be it

Resolved, That the Association of Official Agricultural Chemists by this token express the highest appreciation of the work of our departed member and friend and the deepest sorrow over our irreparable loss; be it further

Resolved, That these resolutions be spread upon the minutes of this meeting and published in suitable form for distribution among our members and the other food chemists, and that a copy be sent to Mrs. Leach.

[Signed] H. W. Wiley, *Chairman.*
H. C. Lythgoe.
A. L. Winton.

REPORT OF AUDITING COMMITTEE.

The committee appointed to audit the accounts of the treasurer would respectfully report that they have examined the same and find them to be correct.

[Signed] Chas. S. Cathcart.
Andrew J. Patten.
H. B. McDonnell.

The report in brief was as follows, detailed statement, vouchers, etc., being filed with the records of the secretary:

Bill of July 29, 1909, for printing and postage (notices)	$13.50
Bill of Aug. 10 and 12, for printing and postage (notices)	10.80
Miscellaneous postage (receipts)	.23
Total expenditures, 1909, 1910	24.53
Receipts (dues of $2 each from 34 stations and colleges, boards of health, etc.)	68.00
Balance	43.47

The report was accepted and the secretary authorized to apply the balance on a printing bill incurred by the committee on food standards.

Mr. Winton, on behalf of Committee C, presented a supplementary report recommending the adoption of the Gorter method for the determination of caffein in coffee instead of the Hilger and Fricke method, which was carried. It was also ordered that the associate referee on cereal products be requested to pay special attention to the examination of wheats and flour, Bulletin 107, Revised, containing only a blank page under this heading, and that milling and baking tests be made. (See report of Committee C, p. 119.)

REPORT ON ORGANIC AND INORGANIC PHOSPHORUS IN FOODS. (SUMMARY.)

By H. S. Grindley, *Associate Referee*, and E. L. Ross.

(A) The water extracts of raw beef were used. The inorganic phosphorus was determined directly by three methods—the Forbes magnesia mixture method,[1] the Emmett and Grindley method,[2] and the Siegfried and Singewald method.[3]

The total phosphorus was determined directly by ashing, digesting with concentrated nitric acid for four hours on the water bath, and then continuing according to the official method. The following table gives the results obtained by the three methods:

Table 1.—*Comparison of the three methods on water extracts of beef.*

[Expressed in per cent of the fresh substance.]

Determination and method.	Beef rib.	Beef round.	
		No. 1.	No. 2.
	Per cent.	*Per cent.*	*Per cent.*
Total phosphorus	0.116	0.137	0.155
Inorganic phorphorus by—			
Emmett and Grindley method	.108	.106	.131
Forbes magnesia mixture method	.103	.104	.133
Siegfried and Singewald method (25 cc barium nitrate)	.103	.104	.131

[1] Ohio Agr. Exp. Sta., 1903, Bul. 215, p. 484.
[2] J. Amer. Chem. Soc., 1906, 28: 26.
[3] Zts. Nahr. Genussm., 1905, 10: 521.

(B) The effect of dilution was investigated in the case of the Siegfried and Singewald method and was found to be negligible. The same volume of extract was used each time and diluted as shown in the following table:

TABLE 2.—*Effect of dilution.*

[Expressed in per cent of fresh substance.]

Determination and method.	Water extracts of beef chuck.	
	No. 1.	No. 2.
	Per cent.	*Per cent.*
Total phosphorus	0.127	0.157
Inorganic phosphorus by—		
Forbes magnesia mixture method (100 cc extract)	.096	.....
Siegfried and Singewald method (25 cc barium nitrate; 100 cc extract	.094	.084
Siegfried and Singewald method (25 cc barium nitrate; 100 cc extract diluted to 500 cc)	.093	.085

(C) The point as to the transformation of organic phosphorus into inorganic phosphorus by heating on the water bath was investigated, and the results show no change of this nature. The heating was carried out as in the Emmett and Grindley method.

TABLE 3.—*Effect of heat on the forms of phosphorus.*

[Expressed in per cent of fresh solution.]

Determination and method.	Water extracts of—		
	Beef round, No. 3.	Beef shank, No. 1.	Beef chuck, No. 2.
	Per cent.	*Per cent.*	*Per cent.*
Total phosphorus	0.149	0.125	0.157
Inorganic phosphorus by—			
Forbes magnesia mixture method before coagulation	.109	.....	.....
Forbes magnesia mixture method after coagulation	.107	.098	.....
Siegfried and Singewald method before coagulation	.104	.....	.084
Siegfried and Singewald method after coagulation	.....	.....	.087
Emmett and Grindley method after coagulation	.105	.097	.....

(D) A study of the effect of using varying amounts of the precipitating agent and the effect of the presence of organic matter in the sample was made. Five cubic centimeters of 10 per cent barium chlorid solution is theoretically more than sufficient to precipitate all the phosphorus in the sample taken. However, from the work of Francis and Trowbridge,[1] the question arose as to whether the amount was actually sufficient to overcome the inhibiting tendencies of the organic matter in the sample. A number of determinations were made upon extracts, before and after the protein was removed. Portions 5, 10, 25, and 50 cc of 10 per cent barium chlorid solutions were used as precipitating agents on the unaltered extracts and on extracts from which the protein was removed, as in the Emmett and Grindley method. The results seem to show that the protein in the water extracts is sufficient to prohibit the precipitation of all of the inorganic phosphorus by means of 5 or 10 cc of 10 per cent barium chlorid solution.

[1] J. Biol. Chem., 1910, 7: 481–501; 8: 81–93.

TABLE 4.—*Effect of the presence of protein material.*

Determination and method.	Sample with protein.			Sample without protein.
	Beef round, No. 4.	Beef shank, No. 1.	Beef round, No. 5.	Beef round, No. 5.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Total phosphorus	0.149	0.125	0.154	.....
Inorganic phosphorus by—				
Emmet and Grindley method	.105	.097	.....	.....
Forbes magnesia mixture method	.109	.....	.....	.....
Siegfried and Singewald method:				
Using 5 cc of 10 per cent barium chlorid	.....	.019	.013	0.075
Using 10 cc of 10 per cent barium chlorid	.013	.023	.014	.082
Using 25 cc of 10 per cent barium chlorid	.095	.078	.086	.083
Using 50 cc of 10 per cent barium chlorid	.104	.....	.086	.084

It appears from these data, first, that the Forbes magnesia mixture method, the Emmett and Grindley method, and the Siegfried and Singewald method give the same results. Second, that the said methods are applicable to dilute as well as to concentrated solutions. Third, that the removal of protein from the solution, as in the Emmett and Grindley method, does not change the form of the phosphorus. Fourth, that a large excess of the precipitating agent must be used to overcome the inhibiting tendencies of the protein in solution.

COLOR OF FLOUR AND A METHOD FOR THE DETERMINATION OF THE "GASOLINE COLOR VALUE."[1]

By A. L. WINTON.

NATURE OF THE COLOR OF FLOUR.

The color of flour is due (1) to mechanical impurities, such as bran particles, weed seeds, dirt, etc., and (2) to the yellow coloring matter associated with the oil, or else extracted by the same solvents, which may be designated for convenience "oil-soluble color."

Mechanical impurities.—The amount of mechanical impurities is dependent to some extent on the nature of the wheat, its soundness, and purity, but chiefly on the grade of flour and the perfection of the milling process, the latter involving both the nature of the milling machinery and the skill of the miller. Of the flour produced at the same mill and from the same run of wheat, the patent is lighter than the clear, because it is practically free from mechanical impurities, its color being due to the oil-soluble color.

Oil-soluble color.—The intensity of the color is dependent chiefly on the kind of wheat. The so-called "yellow-berry" of Nebraska, said to be a degenerate form of Turkey red winter wheat, and durum wheat are examples of varieties which yield flour of a pronounced yellow color, while the soft wheat varieties grown in Michigan, the States adjoining the Ohio River, Washington, and other regions represent the other extreme, the flour being of remarkable whiteness. The hard spring wheats of the Northwest are intermediate as regards color, and it is to meet the competition of the whiter flour from this wheat that the yellow Nebraska and Kansas flours are bleached with nitrogen peroxid. The amount of oil-soluble color in a clear may be no more or even less than in a patent, notwithstanding its higher oil-content. Apparently this is because the oil of the hard endosperm is of a more intense color than that of the bran or the germ, although present in smaller amount.

[1] For details of this report see J. Biol. Chem., 1910, 6: 8.

Effects of extraction.—In order to learn to what extent the oil-soluble color influences the color of the flour and bread, a quantity of a Minnesota patent of a decidedly yellow color was extracted by several portions of ether until the color was removed, after which the residue was air-dried. The extracted flour and the bread made from it were dead white; in fact, were pronounced by expert bakers and millers to be the whitest they had ever seen. The flour resembled powdered starch, not only in color but in mechanical condition. Although it contained 10.28 per cent of moisture, it was loose, lacked coherence, and could not be slicked for pekarizing. The flour did not suffer in rising properties by the extraction, the volume of loaf, after making due allowance for the loss of fat and moisture, being practically identical with that of the bread from the untreated flour. It was, however, lacking in flavor, whereas the bread made from the untreated flour had a rich, nutty flavor. From these results we may conclude that not only the color, but also the coherence and flavor of high-grade flour are largely due to the ether extract, a constituent usually regarded as of minor importance.

Yellow versus White Flour.

The present demand for white flour, that is, flour that is not only free from mechanical impurities, but contains the minimum amount of oil-soluble color, seems irrational. A decided creamy color is a mark of richness and nutty flavor, whereas a dead white is suggestive of an excess of starch and lack of flavor. It is a general fact that the flours with higher gluten content, such as those from hard and durum wheat, are yellower, as a class, than those from the soft wheats with low gluten content, although this is not because the gluten itself is the carrier of the color. These statements, however, apply only to natural flour; bleaching quite destroys these color distinctions between soft and hard wheat and between wheats from different regions and also gives to a clear or straight flour the semblance of a patent. The whiteness produced in this manner is a distinct mark of inferiority, for bleaching not only reduces the wholesomeness of the flour, but injures its flavor. Whatever views may be held with regard to the most desirable color of flour or the merits of bleaching, it can not be denied that the oil-soluble color is a most important commercial quality, not only for æsthetic reasons, but as an indication of strength or of bleaching.

Color Tests.

Pekar's test, although of great value, has its limitations. It is exceedingly difficult to secure definite standards for comparison, as flour continually grows whiter on keeping. Again, it is not practicable to express in numerical terms the difference in color between the standard and the sample under examination. The scoring of experts at best is approximate and strongly influenced by the personal element. The Lovibond tintometer has been adapted for determining numerically the color of flour, but this instrument lacks the necessary delicacy for the purpose and is especially difficult to operate in a poor light. It fails to bring out differences evident on pekarizing.

No direct method is at present available for determining the color due to mechanical impurities and thereby distinguishing between the different milling grades, although the amount of these mechanical impurities is, to a certain extent, directly proportional to the amount of ash, fiber, fat, and protein. As a practical means of distinction the per cent of ash is the most reliable and is quite generally depended on in determining the milling grade.

Methods for determining the amount of oil-soluble color have also been lacking, although a qualitative gasoline test for the amount of this color was suggested by Winton and Shanley[1] as a test for bleaching, corroborating the nitrite test. This test, while of value, especially if the source of the flour and its age are known, is subject to the same objection as the pekarizing process in that it does not give numerical results.

[1] U. S. Dept. Agr., Bureau of Chemistry Bul. 122, p. 217.

Gasoline Color Value.

This method represents an evolution of the qualitative gasoline test. Its chief value is in the comparison of patents or other high grade flours which owe their color to the kind of wheat, not to mechanical impurities, and as a means of detecting bleaching. *It is distinctly a process for determining the oil-soluble color and not the total color or the color due to mechanical impurities.*

Method.—Place 20 grams of the flour in a wide-mouthed, glass-stoppered bottle of about 120 cc (4 ounces) capacity, and add 100 cc of colorless gasoline. Stopper tightly and shake vigorously for 5 minutes. After standing 16 hours, shake again for a few seconds until the flour has been loosened from the bottom of the bottle and thoroughly mixed with the gasoline, then filter immediately on a dry 11 cm paper into an Erlenmeyer flask, keeping the funnel covered with a watch glass to prevent evaporation. In order to secure a clear filtrate, a certain quantity of the flour should be allowed to pass over onto the paper and the first portion of the filtrate passed through a second time. It will be found convenient to fit the filter paper to the funnel by means of water and dry thoroughly either by standing overnight in a well-ventilated place or by heating.

Determine the color value of the clear gasoline solution in a Schreiner colorimeter, using for comparison a 0.005 per cent water-solution of potassium chromate. This solution corresponds to a gasoline number of 1.0 and is conveniently prepared by making 10 cc of a 0.5 per cent solution up to 1 liter. The colorimeter tube containing the gasoline solution should first be adjusted so as to read 50 mm, then the tube containing the standard chromate solution raised or lowered until the shades of yellow in both tubes match. The reading of the chromate solution divided by the reading of the gasoline solution gives the gasoline color value.

Usually the gasoline solution is a true yellow, but sometimes, especially in the case of clear flour, a slight brownish tint is discernible, although this is not sufficient to seriously interfere with the accuracy of the test. Standing for a longer time than prescribed above does not appear to affect the results; in fact, the filtration may be dispensed with entirely if the solution is allowed to settle after the second shaking until perfectly clear, which usually requires at least twenty-four hours.

If desired, the color value may be determined in Nessler tubes, using for comparison potassium chromate solutions of various dilutions prepared from the 0.5 per cent stock solution and filling the tubes in all cases to the height of 50 mm, or (less accurately) in a Lovibond tintometer. In the latter case the color value is obtained directly, the 0.005 per cent potassium chromate solution corresponding in color to the 1.0 yellow slide. In order to avoid the complication of two standards, the color value should in all cases be referred to the 0.005 per cent potassium chromate solution.

If an approximate result is sufficient for the purpose, such may be obtained by carefully pipetting off the clear, supernatant gasoline solution before the second shaking.

The results thus obtained are about 10 per cent lower than by the standard method as above given.

Influence of Variety, Grade, Aging, and Bleaching on the Gasoline Color Value.

In Table 1 are given the gasoline color values of patent and clear flours of four typical kinds of wheat, unbleached and bleached, new and aged for different periods. These are selected from the results obtained on samples representing the two grades of flour from fifteen kinds of wheat. For comparison analyses of the new unbleached flours, made for the most part by Miss H. L. Wessling, are given in Table 2.

TABLE 1.—*Effect of variety, grade, aging, and bleaching on the gasoline color value.*

Description of samples.	Minnesota hard spring.		Nebraska hard winter.		Michigan soft winter.		Missouri soft winter.	
	78 per cent patent.	22 per cent clear.	80 per cent patent.	20 per cent clear.	80 per cent patent.	20 per cent clear.	40 per cent patent.	60 per cent clear.
Unbleached:								
New (February)	2.00	2.00	2.63	2.50	1.43	1.61	1.47	1.60
Aged 10 weeks	1.78	1.82	2.12	2.17	1.22	1.49	1.22	1.33
Aged 20 weeks	1.20	1.34	1.36	1.68	.80	1.20	.68	.88
Aged 30 weeks	.72	.88	.70	.82	.56	.72	.48	.52
Bleached: [1]								
New (February)	.60	.66	.80	.80	.40	.50	.32	.40
Aged 10 weeks	.44	.54	.46	.48	.20	.38	.22	.26
Aged 20 weeks	.30	.50	.34	.40	.20	.36	.18	.24
Aged 30 weeks	.30	.50	.24	.36	.18	.40	.14	.16

[1] All the samples contained, when freshly bleached, approximately 2 parts of nitrous nitrogen per million. After aging 30 weeks nearly all the nitrous nitrogen had disappeared.

TABLE 2.—*Chemical composition of samples of new flour employed in color experiments (Table 1).*

Determinations.	Minnesota hard spring.		Nebraska hard winter.		Michigan soft winter.		Missouri soft winter.	
	78 per cent patent.	22 per cent clear.	80 per cent patent.	20 per cent clear.	80 per cent patent.	20 per cent clear.	40 per cent patent.	60 per cent clear.
Moisture	13.74	13.26	13.33	12.85	13.22	12.62	12.27	12.02
Ash	.44	.85	.39	.67	.42	.89	.39	.50
Crude fiber	.06	.26	.18	.24	.19	.27	.34	.38
Protein (N×5.7):								
Total	10.60	11.74	10.09	11.86	8.66	12.26	9.01	10.72
Alcohol-soluble	5.84	6.21	5.79	6.55	5.24	5.53	5.04	6.21
Salt-soluble	1.62	2.19	1.48	2.02	1.45	2.19	1.25	1.43
Gluten:								
Moist	36.93	38.76	30.48	42.50	20.23	31.24	17.90	33.21
Dry	12.48	13.41	9.85	13.08	6.97	10.55	5.90	10.22
Nitrogen-free extract	74.07	71.91	75.16	73.06	76.40	72.19	77.12	75.23
Fat	1.09	1.98	.85	1.32	1.11	1.77	.87	1.15
Acidity calculated as lactic	.108	.230	.081	.158	.110	.250	.063	.095

Variety of wheat.—It will be noted that the gasoline color value of the new flour from Nebraska hard winter wheat is nearly twice that of Michigan or Missouri soft winter wheats, while that of the Minnesota hard spring wheat is intermediate. These do not, however, represent the extreme figures. The flour was not milled until February, the wheat having aged for from five to six months, during which period the yellow color had probably undergone a certain degree of natural bleaching, although not nearly to the same extent as if the flour itself had been aged for that length of time. The maximum color value for American flour will certainly not be less than 3 and possibly considerably higher. The minimum value has tentatively been placed at 1 for flour examined within 10 weeks after milling. Naturally this minimum figure would be found in a soft wheat flour.

Grade of flour.—The patents and clears from the same milling do not differ appreciatively from each other in gasoline color value. Notwithstanding the higher per cent of fat in the clear, the color value is in one sample the same, in one sample less, and in two samples slightly more than that of the patent. It follows that the oil of the hard endosperm must have a deeper yellow color than the oil of the germ and the outer layers of the kernel. Determinations of gasoline color value of the different wheat products corroborate this statement.

Aging.—The lowering of the gasoline color value during the winter months was so gradual as to be distinctly apparent only after 10 weeks. During the summer months the rate of whitening was more rapid. After 30 weeks about three-fourths of the color had disappeared. As the samples were stored in 12-pound bags at room temperature, it is believed that the figures obtained represent the maximum effect of aging as encountered in the practice. If stored in large bags or barrels or in a cooler place the aging would doubtless have proceeded more slowly.

Bleaching with nitrogen peroxid, to the extent practiced in this experiment (two parts of nitrous nitrogen per million), immediately produced about the same degree of whitening as aging 30 weeks. Aging of the bleached flour brought about further bleaching, so that after 30 weeks hardly any color remained.

If the flour is known to have been milled within 10 weeks the gasoline color value may be depended on to corroborate the determination of nitrous nitrogen as a means of detecting bleaching. If, however, the flour has aged for a much longer period the gasoline color value of a natural flour may drop to 1 or less and the nitrite-reacting material of bleached flour partly or entirely disappear. In such cases it is invaluable to know something of the history of the flour.

REPORT ON THE SEPARATION OF MEAT PROTEIDS.

By C. R. Moulton, *Associate Referee.*

There has been no cooperative work done this year, but the separation of nitrogenous bodies has been continued in the Missouri laboratories in connection with work on concentrated beef extracts and cold-water extracts. We have experienced some difficulty in getting good duplicate results for nitrogen in the case of beef extracts when samples of about 2 grams were weighed out for total nitrogen and digested by the modified Kjeldahl method. When digestion was complete the samples were made up to volume and a one-fifth aliquot was taken for distillation. It seems that when as large a sample as 2 grams is taken it is difficult to get a complete digestion of the nitrogenous bodies. Part of the work was repeated, using about 0.5-gram sample for the digestion. The entire sample was used for distillation of nitrogen. In all cases with the small samples the duplicates were very good, showing that a small sample of beef extract is readily oxidized by the Kjeldahl method, when a larger sample is not. The following table is presented to show the data obtained on a few of the samples:

Percentages of nitrogen in beef extracts using large and small samples.

Sample number.	2-gram sample.	0.5-gram sample.
152 a	10.51	7.90
152 b	10.04	7.92
153 a	12.52	8.72
153 b	9.34	8.72
159 a	10.38	6.73
159 b	8.58	6.64
160 a	10.17	8.49
160 b	7.37	8.60

That the use of a one-half-gram sample should give lower nitrogen results than the use of the 2-gram sample is at first glance surprising, but incomplete hydrolysis during digestion frequently causes the distillate to contain some organic bodies, which obscure the color changes of the cochineal indicator. In such cases the titrations may be either too low or too high.

The referee would recommend that a special study be made of the hydrolytic cleavage products of the nitrogenous bodies in beef extracts in order to determine what bodies resist the Kjeldahl digestion when a large sample of beef extract is used. He recommends also cooperative tests with the Kjeldahl method applied to beef extracts, with a view to determining the best conditions for complete digestion. He further recommends continued cooperative work on the separation of meat proteins in beef extracts. The results reported last year show that various investigators get strikingly different results for the amount of the different nitrogenous bodies present. A perfection or modification of the method should be sought, otherwise no comparison is possible of the results of the different investigators.

Mr. G. E. Patrick submitted two recommendations in regard to methods for the examination of dairy products (the Roese-Gottlieb method for the determination of fat in milk and milk products, and the modified Schmidt-Bondzynski method for the determination of fat in cheese), which were referred to Committee B (see p. 169).

REPORT ON THE SEPARATION OF VEGETABLE PROTEIDS.

By R. Harcourt, *Associate Referee.*

Plan of Investigation.

The work undertaken this year was the separation of the salt-soluble and alcohol-soluble proteids in flour. For this purpose three samples of flour were selected. A and B represented an 85 per cent, or long patent, from the Manitoba wheats of the crops of 1908 and 1909, respectively, and C represented a like proportion of the flour from Ontario winter wheat of 1909. The flours differed widely in quality. Sample A contained less gluten, absorbed less water, and made a smaller loaf of bread, much poorer in texture and in general appearance, than B. This was characteristic of the flour of the two crops of wheat. Sample C was a soft flour, rarely used alone by the commercial bread maker, because it is impossible to produce a large salable loaf of bread from it. The following table will serve to bring out more clearly the difference in the nature of the flours. The baking tests were made by an experienced flour tester, who has all the modern apparatus for making accurate tests.

Results of baking tests on referee's samples of flour.

Data.	1908 hard spring wheat (A).	1909 hard spring wheat (B).	1909 soft winter wheat (C).
Weight of flour (grams)	340	340	340
Wet gluten (per cent)	34.09	38.57	28.80
Absorption (per cent)	67.1	67.6	47.6
Yield of bread (grams)	511	516	478
Volume of loaf (cc)	2,540	2,800	1,780
Color	100	100	.....
Texture	100	103	.....
Appearance	100	105	.....

The object of the work was to determine whether the prescribed methods of separation of the proteids indicate any reason for the difference in the quality of the flours.

The method sent to each of the collaborators was as follows:

Method A.—Total nitrogen determined by the Kjeldahl method.

Method B.—Salt-soluble nitrogen: Place 15 grams of flour in a 500-cc erlenmeyer. Add 300 cc of 10 per cent sodium chlorid solution. Keep at 30° C., shaking at intervals of 10 minutes for 2 hours. Let stand 1 hour. Pipette from the clear supernatant liquid two aliquots of 100 cc each into filter. Refilter, if necessary, until clear. Finally,

wash filter paper with 10 per cent salt solution. Place filtrate in Kjeldahl digestion flask, add 5 cc of concentrated sulphuric acid, and evaporate nearly to dryness. Add remainder of acid necessary for oxidation and determine nitrogen by the Kjeldahl method.

Method C.—Alcohol-soluble nitrogen: Place 5 grams of flour in an Erlenmeyer flask. Add 250 cc of 70 per cent alcohol by volume. Shake at intervals of 30 minutes for 3 hours. Let stand for 18 hours. Draw off two aliquots of 100 cc each, filter till clear and wash with 70 per cent alcohol. Place in digestion flask, add 5 cc of sulphuric acid and evaporate nearly to dryness. Add remainder of acid for oxidation and determine nitrogen by the Kjeldahl method.

Duplicate extractions.

Duplicate nitrogen determinations in each extraction.

Analytical Results.

The following chemists completed the prescribed work and made full reports: Burton J. Ray, Raleigh, N. C.; George A. Olson, Pullman, Wash.; B. R. Jacobs, Bureau of Chemistry, Washington, D. C.; and L. D. Jackson, Guelph, Canada. The results are as follows:

Results of cooperative work on flours.

Sample and determination.	Jackson.	Jacobs.	Olson.	Ray.
Sample A:	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Total nitrogen	2.10	2.02	2.06	2.05
	2.10	2.02	2.07	2.09
	.....	2.02	2.09	.....
	.....	.....	2.07	.....
Salt-soluble nitrogen	.36	.34	.32	.33
	.35	.32	.32	.30
	.37	.34	.33	.29
	.35	.33	.32	.27
Alcohol-soluble nitrogen	1.07	1.18	1.11	1.21
	1.07	1.18	1.11	1.16
	.....	1.14	1.11	1.15
	.....	1.14	1.11	.....
Per cent of total nitrogen:				
Soluble in salt solution	17.1	16.3	15.5	16.0
Soluble in alcohol	51.00	57.44	53.77	56.66
Sample B:				
Total nitrogen	2.19	2.13	2.16	2.19
	2.19	2.13	2.18	2.18
	.....	.....	2.19	2.20
	.....	.....	2.16	.....
Salt-soluble nitrogen	.37	.32	.32	.35
	.38	.32	.30	.32
	.39	.34	.31	.31
	.37	.....	.32	.....
Alcohol-soluble nitrogen	1.13	1.28	1.23	1.19
	1.13	1.26	1.23	1.21
	.....	1.28	1.21	1.24
	.....	1.25	1.20	1.15
Per cent of total nitrogen:				
Soluble in salt solution	17.3	15.0	14.3	15.5
Soluble in alcohol	51.34	59.15	56.46	54.65
Sample C:				
Total nitrogen	1.53	1.49	1.47	1.52
	1.53	1.49	1.47	1.50
	.....	1.49	1.47	.....
	.....	.....	1.47	.....
Salt-soluble nitrogen	.31	.29	.28	.29
	.32	.28	.28	.28
	.31	.27	.29	.29
	.31	.28	.28	.28
Alcohol-soluble nitrogen	.80	.86	.81	.89
	.80	.82	.83	.85
	.80	.84	.81	.86
	.....	.84	.82	.82
Per cent of total nitrogen:				
Soluble in salt solution	20.4	18.8	19.1	18.5
Soluble in alcohol	52.22	56.51	55.90	56.62

Comments of Analysts.

Burton J. Ray, Raleigh, N. C.: Method B: I would suggest that wherever possible constant shaking be substituted for intermittent, as most every laboratory now owns a shaking machine of some kind which will serve the purpose. Where one has, for example, to shake every 10 minutes for a space of 2 hours, it practically takes the man's whole attention for that period, whereas a constant shaking for a shorter or longer period would require no attention except a check on the total time.

"Pipette from the clear supernatant solution." At the end of 1 hour the supernatant liquid is turbid, and when pipetted off and filtered it goes through as turbid as before, even after a dozen refilterings. I found that by shaking up the mass and taking the suspension in an aliquot, one refiltering would give a perfectly clear solution. It is a bit slower in running through, but in the end saves an immense amount of time. This suggestion then fits in with the above: "After shaking constantly for the stated period, pipette off the aliquot, and filter through a dry filter, refiltering as soon as the filtrate begins to come through clear."

"Add 5 cc of concentrated sulphuric acid." Would suggest that the total be added at once (25 cc usually is enough). When evaporated nearly to dryness and "the remainder of the acid necessary" is added, a very troublesome evolution of hydrochloric gas attended by foaming occurs, as the sodium chlorid has separated in solid form. When the total acid is added at once, one does not notice the evolution of hydrochloric acid at all and there is usually much less foaming.

B. R. Jacobs, Washington, D. C.: It is rather difficult to pipette off 200 cc of liquid from 300 cc when there is such a large amount of residue. The first portion pipetted is taken from the upper part of the liquid and the second portion is taken from the lower part, which always carries with it small particles of the flour. The liquid after standing 2 hours without shaking is not homogeneous, and this, in my estimation, constitutes an objection to this method of pipetting. I did not have enough flour to make salt-soluble extractions with 1 and 2 per cent salt solutions, but have made some comparative determinations, using 1 per cent, 2 per cent, 5 per cent, and 10 per cent salt solutions and obtained practically the same amount of nitrogen in each case. The lowest concentration—that is, the 1 per cent salt solution—filtered more rapidly than the rest and gave a clearer filtrate.

Recommendations.

To perfect the method of separating these proteid bodies your referee recommends—

(1) That in the method for the determination of salt-soluble nitrogen all words from "add 5 cc of concentrated sulphuric acid" to "necessary for oxidation" be omitted.

(2) That the influence of the strength of salt solutions on the proportion of nitrogen dissolved be made a matter of study.

(3) That the work of separating the various proteins be carried out in conjunction with actual baking trials.

The results indicate that the method is a workable one; but when we compare the data obtained with the baking tests it is apparent that the former do not furnish much information as to why one flour is superior to another. The total protein does vary with the baking quality of the flours, but the percentage of it in the gliadin, or alcohol-soluble form, is practically the same in all cases, and, therefore, apparently the results are of no value in judging of the strength of the flour. If this phase of the subject is to be followed up I would suggest that the work of Prof. T. B. Wood, Cambridge University, England, be studied, to ascertain if he is correct in his contention that the size of the loaf of bread is influenced by the amount of diastase native to the flour and that the quality of the gluten is affected by the nature of the inorganic salts present.

REPORT ON FOODS AND FEEDING STUFFS (DETERMINATION OF ACIDITY OF FEEDS).

By G. M. MacNider, *Referee.*

The problem of the determination of the acidity of feeds was first brought out by Street in an article read before the association in 1908 and published in the Proceedings for that year. Before taking up the cooperative work a brief résumé of some of the literature will not be out of place.

Quoting from Street's [1] article, "the acidity of a cattle feed may come from a mineral acid used in its preparation, from organic acids natural to the product itself or developed by fermentation during its preparation, and possibly in some cases from phosphates having an acid reaction and normally present in the feed." Osborne's [2] work on the proteins has shown that they are not neutral bodies and that the acidity produced by them is a notable factor when the different indicators are taken into consideration. This will be taken up later.

Gluten feeds have been the chief ones to be investigated, as the process of their manufacture makes it possible for free acid to be left in them during their preparation. Hart and Andrews [3] state that "our commercial feeds of vegetable origin do not contain appreciable quantities of phosphorus in inorganic combination." Ensilage is an example of a feed containing considerable amounts of organic acids developed by fermentation.

Referring again to Osborne's work on the proteins, he has shown that certain protein solutions when neutral to litmus are acid to phenolphthalein and alkaline to lacmoid. He states that "it is important to know whether litmus can be used to determine the point when all combined acid has been converted into neutral salts of sodium or potassium and all the protein substance has been set free." The chief point in determining the acidity of feeds is the indicator to be used. The varying strengths of the different indicators often cause a wide variation in the results obtained.

In the article just mentioned Street tested the effect of several indicators in determining the acidity of gluten feeds by titrating the water extract with decinormal sodium hydroxid solution. The indicators used were phenolphthalein, litmus paper, methyl orange, Congo red, Günzburg's reagent, and Toepfer's reagent. The author states that the Günzburg and Toepfer tests and Congo red are reliable in determining whether or not free mineral acid is present. "None of the extracts showed any acidity to methyl orange, a result to be expected." Tabulated results are presented of titrations with phenolphthalein, litmus, and the Toepfer test. There is very little difference in the results obtained with phenolphthalein and the Toepfer test, but in each case the results obtained with litmus are considerably lower than either of these two. In conclusion, he says: "The results correspond perfectly with what we should expect if the acidity came from dissociation of protein salts alone, or from salts of weak organic acids."

The acidity of gluten feeds was investigated by Goldsmith [4] at the Massachusetts station. The acidity was determined by shaking 5 grams of the feed with 100 cc of water for 15 minutes and titrating an aliquot portion with decinormal sodium hydroxid solution, using phenolphthalein as indicator. Acidity is reported in terms of per cent of sulphuric acid. Comparative tests were made, using phenolphthalein and methyl orange. In every case the feed gave neutral or alkaline reaction with methyl orange. Determinations were made of chlorids, sulphates, and sulphites. They were found to be present in only very small amounts. The author concludes that "the acidity of

[1] U. S. Dept. Agr., Bureau of Chemistry Bul. 122, p. 161.
[2] J. Amer. Chem. Soc., 1902, 24: 39.
[3] New York (Geneva) Station Bul. 238, p. 181.
[4] Mass. Exper. Stat., 121st Ann. Rept., 1909.

gluten feeds is believed to be due primarily to some form of phosphorus, to a much less degree to the acid salt of sulphuric acid, as well as to traces of sulphites and organic acids." The acidity caused by the proteins is not taken into consideration and the results obtained would indicate that this is the source of most of the acidity found.

Fuller [1] studied the acidity of gluten feeds and reports experiments using phenolphthalein, rosolic acid, and cochineal as indicators. Twenty-five grams of the feed were shaken up with water and allowed to stand overnight. Aliquot portions were then filtered off and titrated with decinormal sodium hydroxid solution. The results varied widely with the different indicators. Phenolphthalein required the largest amount of decinormal sodium hydroxid solution, rosolic acid about one-half the amount required by phenolphthalein, and cochineal about one-third the amount of phenolphthalein. The author states that on account of the presence of protein bodies and various acid salts it is inaccurate to calculate the results as free hydrochloric acid.

R. Fanto [2] suggests that the confusion in the statement of acidity of foods could be obviated by expressing all results in terms of milligrams of hydrogen ions in 100 cc or 100 grams of the substance. When the amount of a definite acid is desired it may be obtained by multiplying the weight of the hydrogen ions by an appropriate factor.

As experiments have shown that the acidity of gluten feeds is not due to added mineral acids or to any one substance, but primarily to the proteins, it would seem advisable not to express the acidity in terms of an acid. When the feed extract is titrated with decinormal sodium hydroxid solution it seems advisable to express the acidity in terms of cubic centimeters of solution used or its equivalent in grams of sodium hydroxid.

In carrying out the instructions to continue the study of the determination of acidity of feeds it was considered advisable to determine the acidity of a variety of these products and to send out for cooperative work three typical gluten feeds. The method used for determining the acidity is as follows: Weigh 10 grams of the sample into a shaking bottle, add 200 cc of distilled water, and shake for 15 minutes. Filter the extract through a folded filter and take an aliquot of 20 cc (equal to 1 gram of sample) for the titration. Dilute with 50 cc of distilled water and titrate with standard decinormal sodium hydroxid solution, using phenolphthalein as indicator.

The results obtained with the various indicators, previously referred to in the literature, indicate that phenolphthalein is the most satisfactory indicator to use for this determination and show about what variations may be expected with the different ones, and therefore no determinations were made using other indicators. This method also possesses the advantage of making the method uniform with other methods of determining acidity in food products.

The length of time necessary to shake the sample in preparing the extract was tested on several samples and it was found that no increase in acidity was obtained by shaking longer than 15 minutes.

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[1] Penn. Dept. Agr., Bul. 175.

[2] Zts. angew. Chem., 1906, 19: 1856.

Amount of protein and acidity of feeds.

No.	Kind of feed.	Protein.	Tenth-normal sodium hydroxid.	No.	Kind of feed.	Protein.	Tenth-normal sodium hydroxid.
		Per cent.	*cc*			*Per cent.*	*cc*
1	Continental gluten feed..	29.19	4.50	9	Cottonseed meal.....	41.63	1.20
2	Gluten feed.....	22.38	.30	10	Cottonseed meal.....	39.25	.80
3	Gluten feed.....	23.38	.30	11	Cottonseed meal.....	39.50	1.20
4	Globe gluten feed.....	26.50	1.90	12	Cottonseed meal.....	24.13	.80
5	Gluten feed.....	23.13	.30	13	Cottonseed meal.....	36.13	.90
6	Crescent gluten feed.....	26.50	3.00	14	Cottonseed meal.....	46.75	1.20
7	Buffalo gluten feed.....	26.38	1.10	15	Mixed wheat feed.....	16.13	.70
8	Gluten feed.....	27.50	1.70				

From this table it will be seen that there is no definite relation between the total amount of protein and the acidity; the wheat feed containing 16 per cent of protein showing more acidity than the gluten feed containing 22 per cent of protein, and the cottonseed meal containing 48 per cent of protein showing less acidity than the gluten feed containing 26 per cent of protein. This variation is no doubt caused by the varying amount of protein dissolved by the water from the different samples. The high acidity of No. 1 is probably caused by some fermentation of the sample, thus producing organic acids.

Samples for cooperative work were sent out to six chemists who signified their desire to cooperate in this work, but results have been received from only three. The results obtained by the method as previously stated are presented in the following table:

Cooperative results on acidity of gluten feeds.

[cc tenth-normal sodium hydroxid.]

Analyst.	Sample No. 6.	Sample No. 7.	Sample No. 8.
R. O. Baird, Oklahoma[1]	3.05	1.13	1.77
E. M. Brese, Wisconsin	3.40	1.50	2.20
C. D. Kennedy, Massachusetts[2]	2.76	.80	1.30
G. M. MacNider, North Carolina	3.00	1.10	1.70

[1] Results are averages of 8 determinations. [2] Results are averages of 3 determinations.

These results show only a fair agreement, but the general conclusions which may be drawn are not affected by this, as the feed high in acidity shows high results in the hands of all four chemists, and similar relations are shown on the other two samples.

The determination of the acidity of a feed is usually of very little importance in determining its value. In some cases, for instance with gluten feeds, where the presence of a mineral acid is suspected, the determination of acidity is of value, and in others where fermentation is likely to affect the value of the feed, as in ensilage, the determination of the acidity will give an indication as to the extent to which the fermentation has progressed. In such cases the method as here given furnishes a rapid means of determining the acidity and answers all the requirements for this purpose.

Recommendations.

It is recommended—

(1) That the following method be adopted provisionally for the determination of acidity in commercial feeds:

Weigh 10 grams of the sample into a shaking bottle, add 200 cc of distilled water and shake for 15 minutes. Filter the extract through a folded filter and take an aliquot of 20 cc (equal to 1 gram of sample) for the titration. Dilute with 50 cc distilled water and titrate with standard decinormal sodium hydroxid solution, using phenolphthalein as indicator.

(2) That the referee make a study of the literature on the amount of protein in the various vegetable products used for feed and report to the association at the 1911 meeting on the advisability of adopting more accurate factors for converting nitrogen into protein than the present factor of 6.25.

Several members of the uniform methods committee of the Society of Cotton Products Analysts and the chemists' committee of the Interstate Cottonseed Crushers Association have requested that I bring to the attention of the association the method of determining fat in cottonseed products now in use by the chemists of these societies, i. e., extracting with petroleum ether boiling below 65° C., and request that the association make a study of this method, comparing it with the present official method. This method is used by the chemists engaged in cottonseed work on account of its rapidity and also because the petroleum ether is much cheaper than ethyl ether. These chemists are anxious to adopt a uniform method that will check with the method used by the official chemists who analyze their products. I therefore recommend—

(3) That the association take up the method of extracting fat with petroleum ether boiling below 65° C. as applied to cottonseed products. (See following paper.)

COMPARISON OF PETROLEUM ETHER WITH ETHYL ETHER FOR DETERMINING FAT IN COTTON PRODUCTS.

By G. M. MacNider.

In September the writer received a request from the uniform methods committee of the Society of Cotton Products Analysts and the chemists committee of the Interstate Cottonseed Crushers Association to bring before this association the method for determining fat in cotton products now used by the chemists of the above-named societies. Recently at meetings of these two committees the question of an official solvent for determining fat received a good deal of attention. The chemists' committee of the Interstate Cottonseed Crushers Association adopted as its official method for the analysis of cotton products gasoline or petroleum ether boiling under 65° C. as the solvent, when oil is to be determined, and when cotton seed or its products are sold as feed then the official (ethyl ether) method of this association is to be used. When a commercial chemist receives a sample, the question arises as to whether oil for mill control work or crude fat (ether extract) is desired.

Some correspondence with members of these committees has resulted in Mr. Smalley, of the Southern Cotton Oil Co., and Mr. Paquin sending out samples of cottonseed meal to members of the two associations for cooperative determinations, using the two solvents, petroleum ether and ethyl ether. The results of this work are given on page 157.

The petroleum ether method as used by the chemists engaged in the analysis of cotton products, is as follows:

Extract from 2 to 5 grams of the meal, without previous drying, for three hours in a Soxhlet apparatus with petroleum ether boiling under 65° C. Then evaporate the ether, weigh the residue, and report as oil.

The advantages of this method over the official method are obvious, namely, that the extraction is made without previous drying, which saves much time, and the extraction itself requires three hours as compared with sixteen hours required by the official method. Another point of very great importance to the commercial laboratory is that the petroleum ether used is redistilled 86° gasoline, which, according to figures furnished by Mr. Smalley, costs about 25 cents per gallon. About 3 quarts of ether boiling at 65° are obtained from each gallon of gasoline, which makes the cost of the ether about 33 cents per gallon. Ethyl ether costs from 85 cents to $1.50 per pound, according to the quality of the product. The amount saved by using petroleum ether amounts to a large sum in laboratories where much of this work is done.

The chemists engaged in the analysis of cotton products are anxious for this association to investigate the petroleum ether method, so that, if possible, a uniform method may be adopted which will make the work of their laboratories comparable with the work of the various control laboratories which analyze their products, without necessitating their reanalyzing the products by the official method before they are put on the market.

Lack of time has prevented a thorough review of the literature, but from a brief review there seems to have been no extended investigations showing which solvent extracts are more nearly the true fat. Wiley states in his Principles and Practice of Agricultural Analysis, volume 3 that "for rigid scientific determinations the petroleum is to be preferred to the ether. It is equally as good a solvent for fats and oils and is almost inert in respect to other vegetable constituents. Ether, on the other hand, dissolves chlorophyll and its partial oxidation products, resins, alkaloids, and the like. The extract obtained by ether is therefore less likely to be a pure fat than that secured by petroleum."

Curtiss in the Connecticut Station report for 1889 compared petroleum benzin boiling at 55°–60°, petroleum benzin boiling at 75°–80° and chloroform for determining fat in feeding stuffs. He states that the petroleum benzin was the most unsatisfactory of all and that chloroform dissolves quite as much chlorophyll as ether does. No proof is found that the extract by benzin represents true fat more nearly than ether extract does.

Caldwell in the Proceedings for 1890[1] reports comparative determinations on hay, middlings, and linseed meal dried in hydrogen and extracted with anhydrous ether and with petroleum ether. He states that "the difference between the two series with anhydrous sulphuric ether and with petroleum ether ranges from 0.24 to 0.48 per cent, and is always in favor of the sulphuric ether. It is plain that anhydrous ether is the best medium for extracting fat. * * * Petroleum ether is not so effective, requiring in the first place a longer time for action and leaving behind, in the second place, a portion of the fat, or of the resin and wax heretofore counted as fat." Patterson in the Proceedings for 1894[2] reports the following average results, comparing ether and petroleum ether, on cottonseed meal: Ether extract 13.34 per cent; petroleum ether extract 13.24 per cent.

From these data it would seem that a comparative study of the value of the two solvents, ethyl ether and petroleum ether, would furnish valuable information, not only as to the proper solvent for cotton products, but for feeds in general.

The following cooperative work was done by commercial chemists and was reported by Mr. F. N. Smalley, of the Southern Cotton Oil Co.

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[1] U. S. Dept. Agr., Bureau of Chemistry Bul. 28, p. 82.
[2] U. S. Dept. Agr., Bureau of Chemistry Bul. 43, p. 159.

Comparison of petroleum ether and ethyl ether for determining fat in cottonseed meal.

Analyst and sample.	Low grade cottonseed meal.		High grade cottonseed meal.	
	Oil by petroleum ether boiling at 65° C. (extracted 3 hours).	Oil by ethyl ether (extracted 16 hours).	Oil by petroleum ether boiling at 65° C. (extracted 3 hours).	Oil by ethyl ether (extracted 16 hours).
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
R. C. Warren	6.30	6.60	7.32	7.40
G. Worthen Agee	5.93	6.47	7.02	7.47
Felix Paquin	6.17	6.45	7.27	7.71
Thos. C. Law	6.16	6.38	7.00	7.12
F. N. Smalley	6.00	6.71	7.20	7.24
	[1] 6.06	.....	[1] 7.22	.....

[1] Extracted 16 hours.

These figures are all averages of a number of determinations. On the low grade meal the greatest difference between the two methods is 0.71 per cent, the smallest 0.22 per cent, average 0.41 per cent in favor of the ethyl ether. On the high grade meal the greatest difference is 0.45 per cent, the smallest 0.04 per cent, average 0.22 per cent, in favor of the ethyl ether. These determinations show, as would be expected, that the ether extracts more material than the petroleum ether, and it remains to be determined which extract represents more nearly the true fat.

In working on these samples one of the chemists, Mr. Agee, after extracting with petroleum ether, dried the sample and extracted it with ethyl ether. The extract obtained in this manner when added to the petroleum ether extract very nearly equals, within the limits of experimental error, the ethyl ether extract. Preliminary tests on this second extract showed very little if any fats, but this work is not conclusive.

When the saving in time and money to the commercial chemist by the use of the petroleum ether method and the value to the chemists of the association of having accurate data on this subject are considered, it seems advisable that the association take up the study of these two solvents. I have therefore recommended that this be made a part of the referee's work for the coming year. (See preceding report, page 152.)

The recommendation in regard to future work was referred to Committee B for consideration.

A MODIFICATION OF THE METHOD FOR CRUDE FIBER.

By Morgan P. Sweeney.

The results obtained by different analysts show considerable variation and indicate that the determination of crude fiber is at present made by an unsatisfactory method. There seems to be no determination in the ordinary routine of agricultural chemistry where variations, due to slight differences in style of apparatus and the individual manipulation of the various workers, are so pronounced as in that of crude fiber. The following is a brief description of a modification of the present official method as now used, the value of which is based on these points: First, that it shortens the time necessary to complete the determination; second, that it eliminates the most difficult and disagreeable part of the present method; third, that the duplicates obtained by the modified method agree more closely than by the official method, showing greater accuracy in the work. A description of the apparatus used is also given.

Place 2 grams of the sample in a wide-mouth Erlenmeyer flask of liter size, inserting a small air condenser in the mouth of the flask to prevent concentration due to the loss of steam. To the sample add 200 cc of a 1.25 per cent solution of boiling sulphuric acid as in the official method. Heat to boiling and after boiling for thirty minutes, treat as follows: Neutralize with a 10 per cent solution of sodium hydroxid, using a few drops of phenolphthalein as indicator, approximately 25 cc of sodium hydroxid are required. Add at once 200 cc of a 2.656 per cent solution of boiling sodium hydroxid and continue the digestion at the boiling point for 30 minutes longer, in the same manner as in the treatment with acid. Then filter the alkaline solution containing the fiber residue through a linen cloth rapidly and wash repeatedly with boiling water. Transfer the fiber residue to a tared platinum Gooch crucible and wash with alcohol and ether. Dry at 100° C. and weigh. Ignite the dried residue and again weigh, the loss in weight giving the weight of fiber.

The method as here described differs from the official method adopted by the Association of Official Agricultural Chemists as follows: Instead of filtering and washing free from acid at the end of the acid digestion, the acid is neutralized. Instead of continuing the digestion in 200 cc of sodium hydrate of 1.25 per cent, 200 cc of 2.65 per cent sodium hydrate is added to the neutral solution, making a total of 425 cc of sodium hydrate, the strength of which is 1.25 per cent, and which contains a small amount of sodium sulphate. Instead of extracting the fat with ether as a first step in the determination, the residue from the digestion is washed in the Gooch crucible on the filter several times with alcohol and then with ether.

The writer has tried the various styles of apparatus in use for the determination of fiber and is of the opinion that the kind described here is as good as can be employed in the process, both from the viewpoint of ease of manipulation and of accuracy. For the digestion the wide-mouth, Erlenmeyer distillation flasks of liter size are used. The necks of these flasks are wound with cord to prevent burning the fingers in handling. A rubber stopper is inserted through which passes a small air condenser of the bulb type. The alkali is filtered through finely woven linen cloth cut into circular pieces about 18 cm in diameter. This cloth is loosely suspended in a funnel about 12 cm in diameter. The edges of the linen are fastened to the top of the funnel with little clasps to prevent it from slipping down to the bottom of the funnel. These clasps can be made readily by bending strips of tin so that they will slip over the edges of the funnel, holding the cloth securely in place. After washing the residue on the linen filter, the cloth is placed upon a tin or sheet-iron plate which has been bent into a "V" shape. This allows the filter to be readily washed into a Gooch crucible with a very small amount of water. In the Gooch crucible is a pad of asbestos, or better still, a platinum felt, protected by a platinum gauze.

Filtering and washing the sample free from acid after the first half hour of boiling has proved a decided loss of time. With many samples it is difficult to filter and wash at all at this point. The residue is often in such a state that it sticks to the filter and prevents the solution and wash water from going through. This, of course, retards the determination and is the cause of a large part of the variations between duplicates and the nonagreement of results by different workers. The time estimated for transferring to the filter, washing free from acid, and returning to the flask for digestion with alkali is from one-half to one and one-half hours, and in some cases even longer. By the proposed method the acid is neutralized, the proper amount of alkali added, and the digestion continued with an interruption of from one to three minutes only. This shortening of the required time is decidedly in favor of the proposed method.

The filtration of the alkaline solution through linen loosely suspended in a large funnel is very rapid. It is entirely satisfactory, and allows a thorough washing with hot water in a much shorter time than any other type of filter tried. The washing of the fiber residue with alcohol and ether on the suction filter, instead of extracting the original sample with ether, has proved very satisfactory. It is also of added convenience in that it aids in drying the crude fiber residue. The other method requires

drying the sample at 110° C. The use of ether in washing the residue leaves the fiber in such a state that it will dry to constant weight in a steam oven at less than 100° C.

Neutralizing the acid with sodium hydrate causes the formation of a small amount of sodium sulphate. Careful and varied tests show no variation in the results, due to the presence of this salt. Its only noticeable effect is that it raises the boiling point of the alkaline solution about 0.2°. The boiling point of the alkali in 10 samples, determined by the official method, varied from 98.9° C. to 99.3° C. The boiling point of the alkali as used in the modified method varied from 99.1° C. to 99.4° C. This slight rise in boiling point is negligible, as the different types of digestion flasks used causes a greater variation in the boiling point, due to difference of surface tension.

The following comparisons of results by each method shows the agreement of the fiber percentage to be close by the two methods. Where duplicates by the same method are given, it will be seen that the checks, as a rule, are closer in the case of the proposed method.

Crude fiber determinations by two methods.

Sample No.	Official method.			Proposed method.		
	Total.	Average.	Variation.	Total.	Average.	Variation.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
746	{ 14.71 14.32 }	14.51	0.39	{ 14.53 14.44 }	14.49	0.09
904	{ 4.70 4.81 }	4.76	.11	{ 4.67 4.80 }	4.74	.13
914	{ 9.88 10.16 }	10.02	.28	{ 9.89 9.92 }	9.90	.03
927	{ 10.45 10.15 }	10.30	.30	{ 10.38 10.38 }	10.38	.00
946	{ 14.06 13.21 }	13.64	.85	{ 13.40 13.48 }	13.44	.08
951	{ 22.76 22.17 }	22.47	.59	{ 22.75 22.51 }	22.62	.24
995	{ 20.73 21.06 }	20.90	.33	{ 20.90 20.65 }	20.77	.25

The following table shows results by three different workers using the official method, also the results obtained by the modified method:

Comparison of results on crude fiber by three analysts using the official method and results by the new method.

Sample No.	Official.			New method.
	Analyst 1.	Analyst 2.	Analyst 3.	
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
2933	5.66	6.05	6.20	6.29
3011	7.42	6.77	7.76	7.40
3067	4.69	4.26	4.92	4.82
738	4.10	.....	.....	4.16
3069	5.42	4.77	5.33	5.67
743	11.04	.....	.....	11.01
3072	2.20	1.48	2.01	2.38

The samples used in making the comparative tests of the two methods included alfalfa, cottonseed meal, gluten, corn bran, wheat bran, ground oats, corn, and hominy. In each case good comparative results were obtained. The checks for duplicates

were, in most instances, best when the results were obtained by the proposed method. It seems only reasonable to conclude that the proposed method is much preferable to those now in use. It gives comparable results, the duplicate checks are closer, the time required for the determination lessened, the most disagreeable part of the method is eliminated, and a great source of error is avoided.

This paper was referred to Committee B for consideration; see page 169.

REPORT ON SUGAR AND MOLASSES.

By H. P. Agee, *Referee*, and R. S. Hiltner, *Associate Referee*.

In planning the cooperative work on sugar and molasses methods the recommendations of a year ago were closely followed. The work was confined largely to moisture methods and the effect of different agents of clarification upon direct and Clerget polarizations. The samples for the work were selected to include a wide range of sirups and molasses in order that the several methods under consideration could be tested upon these products of varying composition. The samples were: No. 11, a Cuban raw sugar. No. 12, a high-grade sirup. No. 13, a high-grade "open-kettle" molasses. No. 14, a centrifugal molasses. No. 15, a mixture of blackstrap and commercial glucose. The following instructions accompanied the samples which were sent to the various cooperators:

Instructions.

MOISTURE.

Determinations to be made on all samples.

(1) Dry 2 grams of material on sand to constant weight in vacuum oven at 70° C. Note number of hours necessary to obtain constant weight.

(2) Dry 2 grams of material on sand in water jacketed oven for 10 consecutive hours.

(2a) Repeat No. 2 without the use of sand.

(2b) Continue drying for 20–30 and 40 hours to note difference in effect on different materials.

(3) By Brix spindle (molasses and sirup only). See Areometric method (1) page 65, Bulletin 107, Revised. (If inconvenient to secure Brix spindle determine specific gravity by Westphal balance and convert to degree Brix, by tables).

(4) Refractometer. Make refractive index reading and convert to percentage moisture by means of the Geerligs tables: (a) In concentrated form; (b) half diluted with water; (c) half diluted with saturated solution of sugar, using formula:

$$X=\frac{(A+B)C-BD}{A}$$

A=Weight of material taken and mixed with B. B=weight of sugar solution. C=per cent dry substance of above mixture obtained from refractive index. D=per cent dry substance of pure solution obtained from refractive reading.

POLARIZATION.

Weigh out a normal weight and make up to 100 cc or to such a multiple thereof as may be necessary to secure an accurate polarization after clarifying as follows:

(1) With lead subacetate solution (Bul. 46, revised, pp. 38–39; also Bul. 107, Revised, p. 40).

(2) With normal lead acetate solution (saturated solution of lead acetate in water.)

(3) With Horne's dry lead subacetate (J. Amer. Chem. Soc., 1904, *26:* 186).

(4) With Herles's solutions: Use equal parts of No. 1 and No. 2. (No. 1=250 grams lead nitrate to 500 cc of water. No. 2=25 grams sodium hydrate to 500 cc of water.)

(5) Repeat the four preceding tests, using double the quantity of clarifying agent.

(6) Determine sucrose by Clerget's method, as given in Bulletin 107, Revised, page 41, with solutions from each of the four clarifications. Use the formula:

$$\text{Sucrose}=\frac{(A-B)}{142.66-\frac{T}{2}}$$

(Record all dilutions and temperatures of polarizations.)

COMMERCIAL GLUCOSE.

(1) Estimate the amount of commercial glucose by the following formula:

$$G=\frac{(a-S)100}{175}$$

where G=per cent of commercial glusose; a=direct polarization; S=per cent of cane sugar as determined by Clerget's method.

(2) Of the samples indicated by (1) to contain commercial glucose, polarize an inverted half-normal solution prepared as directed on page 71 of Bulletin 107, Revised, at 87° C.

Multiply by 2 the reading at 87° C. in the 200 mm tube; multiply this result by 100 and divide by the factor 163 to express the percentage in terms of commercial glucose polarizing 175° V.

It is important that work on samples be commenced as soon as is possible after their receipt on account of changes due to fermentation.

Analytical Data.

Nine chemists contributed results which are herein presented in tabular form:

MOISTURE.

The object of the work that was prescribed on moisture methods was to secure additional data to that which has been accumulated in previous years on the methods which are detailed in the instructions, and to examine further the refractometer method (which has been adopted provisionally by the association) as applied to dark products that necessitate dilution to give a clear reading. The results are presented in Table 1.

TABLE 1.—*Cooperative results on moisture determinations.*

[Percentage results.]

Sample and analyst.	Refractometer.			Drying at 98° C. on sand.			Drying at 98° C. without sand.					In vacuum.	
	Concentrated.	Diluted one-half water.	Diluted sugar solution.	10 hours.	20 hours.	30 hours.	10 hours.	20 hours.	30 hours.	18 days.	100 − °Brix.	Hours.	Per cent water.
Sample 11:													
A. Given	0.87	0.98	.....	0.87	0.98	0.98	0.91	0.98	1.03	.....	.....	27	0.88
R. S. Hiltner	.....	.....	.....	.37	.49	.57	.69	.77	.82	.....	.....	33	.3
W. G. Taggart	.....	.....	.....	.....	.....	.....	.96	1.00	1.02	1.32	.....	57	1.00
H. P. Agee	.....	.....	.....	.....	.....	.....	1.14	1.19	1.22	.....	.....	.....	.....
G. B. Taylor	.....	.....	.....	.64	.66	.....	.67	.56	.....	.....	.....	.....	.....
Average	.....	.....	.....	.63	.71	.77	.87	.90	1.02	1.32	.....	.....	.64
Sample 12:													
A. Given	27.3	26.6	25.95	25.80	28.01	28.45	27.92	28.56	28.96	.....	25.7	27	27.39
R. S. Hiltner	.....	.....	27.2	27.33	28.01	28.35	27.32	28.10	28.39	.....	26.	33	27.44
W. G. Taggart	27.00	26.00	26.84	27.02	27.80	28.02	25.83	27.75	28.33	32.42	27.	57	26.71
M. H. Wiley	.....	.....	.....	27.01	.....	.....	24.60	[1] 26.13	[2] 27.56	.....	26.03	.....	.....
C. A. Browne	27.5	27.2	27.21	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
G. B. Taylor	25.15	24.30	25.55	25.32	27.73	27.17	26.06	27.47	28.22	.....	25.08	.....	.....
H. P. Agee	27.9	26.4	26.83	27.16	27.36	28.35	26.24	27.46	27.89	.....	25.90	.....	.....
Average	26.97	26.10	26.59	26.60	27.78	28.07	26.33	27.58	28.22	32.42	25.95	.....	27.18
Sample 13:													
A. Given	26.10	25.84	21.45	25.36	26.90	27.35	25.83	26.52	26.93	.....	24.30	27	25.65
R. S. Hiltner	.....	.....	26.35	25.93	26.75	27.15	25.77	26.46	26.71	.....	24.9	33	26.03
W. G. Taggart	25.90	24.50	24.84	26.25	26.80	27.43	25.40	26.16	26.39	32.65	24.2	57	27.20
H. P. Agee	26.55	24.20	25.74	26.27	26.83	27.25	25.60	26.20	26.46	.....	24.40	.....	.....
M. H. Wiley	.....	.....	.....	25.39	.....	.....	24.82	[1] 25.20	[2] 25.76	.....	25.10	.....	.....
C. A. Browne	26.30	26.30	26.04	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
G. B. Taylor	22.60	25.50	23.45	24.25	25.33	25.59	24.84	25.79	25.91	.....	25.88	.....	.....
Average	25.49	25.27	24.64	25.57	26.52	26.95	25.37	26.05	26.36	32.65	24.79	.....	26.29
Sample 14:													
A. Given	25.85	25.84	21.65	26.56	27.86	28.27	26.39	27.72	28.16	.....	22.1	27	25.94
R. S. Hiltner	.....	.....	25.85	25.89	27.31	27.69	25.55	27.03	27.50	.....	23.10	33	26.57
W. G. Taggart	25.60	24.30	24.95	27.33	28.27	28.71	25.61	27.16	27.65	33.50	22.22	57	26.01
H. P. Agee	25.80	24.50	25.97	26.90	27.94	28.21	25.62	27.47	27.85	.....	22.48	.....	.....
C. A. Browne	25.8	25.7	25.71	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
G. B. Taylor	23.48	24.55	25.20	25.62	26.73	27.52	25.10	26.59	26.68	.....	23.65	.....	.....
M. H. Wiley	.....	.....	.....	24.87	.....	.....	25.31	[1] 26.05	[2] 26.80	.....	23.30	.....	.....
Average	25.30	24.97	24.89	26.19	27.62	28.08	25.59	27.00	27.44	33.50	23.80	.....	26.17
Sample 15:													
A. Given	20.72	19.70	16.65	22.57	24.70	25.84	22.94	24.86	25.63	.....	16.80	27	20.74
R. S. Hiltner	.....	.....	21.15	21.94	24.10	24.73	21.30	23.43	24.45	.....	18.70	33	22.76
W. G. Taggart	21.70	19.20	21.38	24.01	23.95	24.10	22.19	24.00	24.62	32.78	15.30	52	22.79
H. P. Agee	22.20	19.10	21.54	23.47	24.76	25.18	22.45	24.12	25.15	.....	15.36	.....	.....
M. H. Wiley	.....	.....	.....	22.22	.....	.....	22.42	[1] 23.14	[2] 24.04	.....	17.60	.....	.....
C. A. Browne	21.3	20.2	20.8	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
G. B. Taylor	19.50	17.40	20.05	21.62	23.48	24.31	21.84	23.63	24.08	.....	16.28	.....	.....
Average	21.08	19.12	20.26	22.64	24.19	24.02	22.19	23.86	24.66	32.78	16.67	.....	22.09

[1] Time of drying sixteen hours.

[2] Time of drying twenty-two hours.

The error in diluting an impure sugar solution to determine its refractive index that is due to a contraction in volume was pointed out in the report of the referee of last year. The results obtained in carrying out the recommendation for a study of a pure sugar solution as a diluent in order to reduce this error to a minimum show distinct differences in the majority of cases upon the undiluted material, that which has been diluted with water, and that which has been diluted with sugar solution. The results presented in last year's report (Bulletin 132, p. 178) show a higher content of solids and, consequently, a lower content of moisture in the results by dilution with water than with the undiluted material or with that which was diluted with sugar solution. The

results on four samples by seven chemists in this year's cooperation conform to the work of last year in general. Nevertheless they present such contrarieties in certain instances as to make it inadvisable to pass finally upon the matter without further investigation. The dilution results seem subject to greater variation on the part of the individual analyst than the determinations on the undiluted material.

The results by drying with the weighings made after periods of 10 hours, 20 hours, and 30 hours, bring out very clearly the difficulties in getting accurate results by these methods. The 10-hour results are in every case lower than the 20-hour results, and these in turn are each time lower than the 30-hour results. The work of Taggart, who continued the heating for 18 days and obtained figures indicating from 4 to 8 per cent higher water content, shows the impracticability of obtaining constant weight by these methods.

POLARIZATION.

The work this year was confined to the effect of different clarification agents on direct and Clerget polarizations. The results are given in Table 2.

TABLE 2.—*Cooperative polarization results; using different clarifying agents.*

Clarifying agent and analyst.	Sample No. 11—Sugar.						Sample No. 12—Sirup.					
	Normal quantity clarifying agent.			Excess quantity clarifying agent.			Normal quantity clarifying agent.			Excess quantity clarifying agent.		
	Amount clarifying agent.	Direct.	Clerget.	Amount clarifying agent.	Direct.	Clerget.	Amount clarifying agent.	Direct.	Clerget.	Amount clarifying agent.	Direct.	Clerget.
Lead subacetate:	*cc.*	*P. ct.*	*P. ct.*	*cc.*	*P. ct.*	*P. ct.*	*cc.*	*P. ct.*	*P. ct.*	*cc.*	*P. ct.*	*P. ct.*
A. Given	1.1	96.65	97.20	2.2	96.65	96.99	4.6	52.4	55.33	9.2	53.25	55.29
R. S. Hiltner	1.8	97.16	98.26	3.6	97.16	97.80	4.2	52.33	55.68	8.4	52.88	56.46
W. G. Taggart	1.0	96.4	98.78	2.0	96.30	98.78	1.0	52.1	55.98	2.0	52.20	55.95
H. P. Agee	1.0	96.00	97.98	2.0	96.05	98.10	2.0	52.13	54.68	4.0	52.4	54.84
W. D. Horne	4.0	96.35	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
G. H. Hardin	1.0	96.5	.....	.....	.....	.....	3.0	51.95	54.54	.....	.....	.....
H. W. Dietrich	1.0	96.5	.....	.....	.....	.....	3.0	52.00	54.12	6.0	52.2	54.58
Average	.....	**96.5**	**98.05**	.....	**96.54**	**97.92**	.....	**52.15**	**55.05**	.....	**52.58**	**55.42**
Neutral lead acetate:												
A. Given	1.2	96.55	96.91	2.4	96.50	97.1	4.5	52.1	55.33	9.0	52.5	55.55
R. S. Hiltner	1.4	97.14	98.60	2.8	97.10	98.22	3.3	52.27	56.06	6.6	52.46	56.28
W. G. Taggart	2.0	96.3	98.78	4.0	96.40	98.78	2.0	52.00	55.89	4.0	52.1	56.05
H. P. Agee	2.0	96.05	98.10	4.0	96.15	98.35	4.0	52.1	54.96	8.0	52.2	54.80
G. H. Hardin	.....	.....	.....	.....	.....	.....	4.0	52.03	.....	.....	.....	.....
Average	.....	**96.51**	**98.09**	.....	**96.53**	**98.11**	.....	**52.1**	**55.56**	.....	**52.31**	**55.67**
Horne's dry lead:	*Gms.*			*Gms.*			*Gms.*			*Gms.*		
A. Given	.4	96.60	97.1	.8	96.60	96.94	1.5	52.2	54.95	3.0	52.55	54.91
R. S. Hiltner	1.0	97.20	98.21	2.0	97.00	97.51	2.3	52.7	55.92	4.6	53.54	56.26
W. G. Taggart	.3	96.35	98.78	.6	96.40	98.69	.3	52.00	55.89	.6	52.30	56.29
H. P. Agee	.3	96.10	98.23	.6	96.2	98.31	.5	52.1	54.79	1.0	52.4	55.19
G. H. Hardin	.....	.....	.....	.....	.....	.....	1.0	51.98	.....	.....	.....	.....
H. W. Dietrich	.....	.....	.....	.....	.....	.....	1.0	52.1	.....	2.0	52.25	.....
W. D. Horne	.5	96.20	.....	1.0	96.1	.....	.....	.....	.....	.....	.....	.....
Average	.....	**96.49**	**98.08**	.....	**96.46**	**97.86**	.....	**52.18**	**55.38**	.....	**52.6**	**55.66**
Herles solution:	*cc.*			*cc.*			*cc.*			*cc.*		
R. S. Hiltner	2.8	97.21	98.01	5.6	97.20	98.37	8.2	52.66	56.39	16.4	52.76	56.46
A. Given	1.0	96.70	96.72	2.2	96.50	96.57	3.2	52.45	55.51	6.4	52.95	55.74
W. G. Taggart	2.0	96.30	98.78	4.0	96.35	98.82	2.0	52.20	56.13	4.0	52.2	56.13
H. P. Agee	2.0	96.15	98.45	4.0	96.15	98.10	4.0	52.30	54.94	8.0	52.6	55.44
Average	.....	**96.59**	**97.96**	.....	**96.55**	**97.96**	.....	**52.40**	**55.74**	.....	**52.62**	**55.94**

TABLE 2.—*Cooperative polarization results, using different clarifying agents*—Continued.

Clarifying agent and analyst.	Sample No. 13—Open-kettle molasses.						Sample No. 14—Centrifugal molasses.					
	Normal quantity clarifying agent.			Excess quantity clarifying agent.			Normal quantity clarifying agent.			Excess quantity clarifying agent.		
	Amount clarifying agent.	Direct.	Clerget.	Amount clarifying agent.	Direct.	Clerget.	Amount clarifying agent.	Direct.	Clerget.	Amount clarifying agent.	Direct.	Clerget.
Lead subacetate:	*cc.*	*P. ct.*	*P. ct.*	*cc.*	*P. ct.*	*P. ct.*	*cc.*	*P. ct.*	*P. ct.*	*cc.*	*P. ct.*	*P. ct.*
A. Given	6.8	45.00	48.09	13.6	45.8	48.39	8.5	42.10	45.31	17.0	43.1	45.53
R. S. Hiltner	6.5	45.17	49.16	13.0	45.7	50.13	8.5	42.21	46.83	17.0	43.30	47.61
W. G. Taggart	1.5	45.00	48.6	3.0	45.3	48.92	6.0	42.6	46.12	12.0	43.00	45.74
H. P. Agee	1.0	44.4	49.9	2.0	44.6	50.06	8.0	42.00	47.52	16.0	42.60	47.81
G. H. Hardin	2.0	44.68	47.88	.....	.....	.....	12.0	42.1	45.66	.....	.....	.....
H. W. Dietrich	4.0	45.00	48.09	8.0	44.7	.....	12.0	42.20	45.68	24.0	42.60	.....
Average	.....	**44.87**	**48.62**	.....	**45.22**	**49.37**	.....	**42.21**	**46.18**	.....	**42.52**	**46.67**
Neutral lead acetate:												
A. Given	7.0	44.9	48.09	14.0	45.00	48.39	7.5	42.00	45.84	15.0	42.00	46.13
R. S. Hiltner	4.7	44.9	48.98	9.4	44.7	48.96	5.6	43.00	47.51	11.2	42.8	48.34
W. G. Taggart	2.5	45.1	48.77	5.0	45.50	48.99	12.0	42.8	46.11	24.0	43.2	45.90
H. P. Agee	2.0	44.45	49.94	4.0	44.60	50.1	16.0	42.00	47.17	32.0	42.2	47.50
G. H. Hardin	2.0	44.51	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
H. W. Dietrich	.....	.....	.....	.....	.....	.....	24.0	41.9	.....	48.0	42.1	.....
Average	.....	**44.77**	**48.94**	.....	**44.95**	**49.11**	.....	**42.34**	**46.66**	.....	**42.46**	**46.97**
Horne's dry lead:	*Gms.*			*Gms.*			*Gms.*			*Gms.*		
A. Given	2.3	44.8	48.09	4.6	45.6	47.34	2.8	42.00	45.23	5.6	42.5	44.1
R. S. Hiltner	2.5	45.03	48.87	5.0	46.11	48.85	3.0	42.08	46.50	6.0	43.50	47.29
W. G. Taggart	.4	45.00	48.78	.8	45.6	49.16	1.2	42.4	45.96	2.4	43.2	46.42
H. P. Agee	.3	44.5	49.98	.6	44.6	49.7	2.0	42.4	47.83	4.0	42.6	47.6
G. H. Hardin	1.0	44.53	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
H. W. Dietrich	1.0	45.1	.....	2.0	45.7	.....	12.0	43.1	.....	14.0	43.4	.....
Average	.....	**44.82**	**48.93**	.....	**45.52**	**48.76**	.....	**42.39**	**46.38**	.....	**43.04**	**46.35**
Herles solution:	*cc.*			*cc.*			*cc.*			*cc.*		
R. S. Hiltner	7.0	44.90	48.92	14.0	45.41	49.03	9.0	42.42	47.88	18.00	42.94	48.13
A. Given	5.0	45 00	48.2	10.0	45.60	48.55	6.5	42.20	45.84	13.00	43.00	44.63
W. G. Taggart	2.0	45.05	48.72	4.0	45.6	49.07	8.0	42.8	45.93	16.00	43.6	46.91
H. P. Agee	2.0	44.50	49.98	4.0	44.7	50.14	16.0	42.4	47.66	32.00	43.2	47.77
Average	.....	**44.86**	**48.95**	.....	**45.32**	**49.19**	.....	**42.45**	**46.82**	.....	**43.18**	**46.86**

TABLE 2.—*Cooperative polarization results, using different clarifying agents*—Continued.

Clarifying agent and analyst.	Sample No. 15—Mixed molasses.					
	Normal quantity clarifying agent.			Excess quantity clarifying agent.		
	Amount clarifying agent.	Direct.	Clerget.	Amount clarifying agent.	Direct.	Clerget.
Lead subacetate:	*cc.*	*Per cent.*	*Per cent.*	*cc.*	*Per cent.*	*Per cent.*
A. Given	15.0	51.6	19.90	30.0	52.6	.....
R. S. Hiltner	15.0	50.92	23.90	30.0	51.32	23.52
W. G. Taggart	10.0	49.6	24.77	20.0	50.2	24.35
H. P. Agee	12.0	51.4	24.31	24.0	52.00	24.78
W. D. Horne	30.0	51.60	.....	60.0	52.50	.....
G. H. Hardin	.....	.....	.....	28.0	51.24	22.89
H. W. Dietrich	28.0	51.4	22.76	56.0	52.1	.....
Average	.....	**51.09**	**23.12**	.....	**51.7**	**23.88**
Neutral lead acetate:						
A. Given	12.0	51.6	.....	24.0	51.6	.....
R. S. Hiltner	10.5	49.2	22.71	21.0	49.7	22.85
W. G. Taggart	12.0	50.00	24.54	24.0	50.00	24.40
H. P. Agee	16.0	51.6	24.12	32.0	52.00	24.43
H. W. Dietrich	56.0	51.00	.....	112.0	51.6	.....
Average	.....	**50.68**	**23.79**	.....	**50.98**	**23.89**
Horne's dry lead:	*Grams.*			*Grams.*		
A. Given	5.0	49.50	21.03	10.0	51.6	.....
R. S. Hiltner	4.0	50.00	23.62	8.0	50.28	23.27
W. G. Taggart	3.2	50.00	24.13	6.4	50.00	24.4
H. P. Agee	3.2	51.6	24.12	6.4	52.00	23.31
H. W. Dietrich	8.0	50.9	.....	16.0	51.50	.....
W. D. Horne	4.0	51.20	.....	8.0	51.60	.....
Average	.....	**50.53**	**23.22**	.....	**51.16**	**23.66**
Herles solution:	*cc.*			*cc.*		
R. S. Hiltner	16.0	50.04	23.57	32.0	50.68	23.58
A. Given	11.0	51.90	21.94	22.0	52.20	.....
W. G. Taggart	16.0	50.00	24.19	32.0	50.00	24.4
H. P. Agee	16.0	51.8	23.86	32.0	52.4	24.41
Average	.....	**50.93**	**23.39**	.....	**51.32**	**24.13**

This work is practically a repetition of last year's investigation except that more samples were studied. Attention was called in last year's report to certain variations in the results due to these different clarifying agents, but the work of this year does not wholly conform to the variations that were brought out last year. Table 3, which presents the final averages and is a condensation of Table 2, shows that there is close uniformity in the results obtained by the four methods of clarification.

TABLE 3.—*Summary of polarization results, using different clarifying agents.*

Clarifying agent and number of sample.	Direct polarization.		Clerget.	
	Normal amount of clarifier.	Excess of clarifier.	Normal amount of clarifier.	Excess of clarifier.
Lead subacetate:	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
1	96.50	96.54	98.05	97.92
2	52.15	52.58	55.05	55.42
2	44.87	45.22	48.62	49.37
4	42.21	42.55	46.18	46.67
5	51.09	51.70	23.12	23.88
Average	57.36	57.72	54.20	54.65
Neutral lead acetate:				
1	96.51	96.53	98.09	98.11
2	52.10	52.31	55.56	55.67
3	44.77	44.95	48.94	49.11
4	42.34	46.65	42.46	46.97
5	50.68	50.98	23.79	28.89
Average	57.28	58.28	53.77	55.75
Horne's lead:				
1	96.49	96.46	98.08	97.86
2	52.18	52.60	55.38	55.66
3	44.82	45.52	48.93	48.76
4	42.39	43.04	46.38	46.35
5	50.53	51.16	23.22	23.66
Average	57.28	57.75	54.39	54.46
Herles solution:				
1	96.59	96.55	97.96	97.96
2	52.40	52.62	55.74	55.94
3	44.86	45.32	48.95	49.19
4	42.45	43.18	46.82	46.86
5	50.93	51.32	23.39	24.13
Average	57.45	57.39	54.57	54.82

In the first column, which gives the direct polarizations without excess of clarifying material, the following figures are found:

	Per cent.
Lead subacetate	57.36
Neutral lead acetate	57.28
Horne's dry lead	57.28
Herles solution	57.45

The "excess" column gives wider variations and the Clerget results even greater deviations, but it is thought that the results as a whole warrant all four clarifying agents being considered as equally reliable. However, it has been proposed that Horne's lead, having the advantage of eliminating the error of the precipitate, be adopted as the sole official method. Additional work to establish the advisability of this step is recommended. Since the dry lead was adopted provisionally last year, it is of interest to quote the following on its use from a report made by W. D. Horne, its originator. He says:

It is desirable in using dry lead to avoid adding much more than is necessary to get a good flocculation and precipitation of coloring matter. Under such conditions the

results obtained are closer to the theoretical results than any other method will produce, but if a larger excess of dry lead is added, new errors will be introduced. Excessive reagent tends to dilute the solution and to lower the reading slightly while at the same time in the presence of invert sugar it tends to precipitate or render optically inactive some of the levulose, thus tending slightly to raise the polarization. While these two small errors tend to compensate each other, it is still desirable from a scientific point of view to avoid incurring them; hence the warning to avoid using excessive amounts of reagent.

On account of other matters in hand no work was done on the effect of different compositions of basic lead subacetate, and therefore the recommendation of last year in this regard is repeated.

A sample containing commercial glucose was included in this year's work at the request of certain commercial chemists who have had occasion to observe the divergent results that have been obtained by certain analysts in the determination of the percentages of commercial glucose in mixed molasses.

TABLE 4.—*Percentage of commercial glucose in sample No. 15.*

Analyst.	Method I.	Method II.
Given	16.89	20.37
Hiltner	15.36	18.93
Taggart	16.04	19.63
Agee	15.71	21.59

The sample under consideration contained 20 per cent of commercial glucose. It will be noted that the results of Method II conform more closely to the percentages actually present. The results of Method I agree fairly well among themselves but are all low on account of the invert sugar present in the black-strap molasses. Method I, using direct polarization and factor 175, can only be used where there is little or no invert sugar present. Invert sugar lowers the direct polarization and hence when the per cent sucrose is subtracted and the result divided by 175, the percentage of commercial glucose obtained is too low.

RECOMMENDATIONS.

It is recommended—

(1) That further work be done on the Horne dry-lead clarification with the view to ascertaining whether it is advisable to adopt it as the sole official method.

(2) That a study be made of the effect of variation in polarizations due to the composition of the basic lead acetate (Browne, Bul. 122, p. 223).

(3) That the moisture determination by refractometer be further studied, with special reference to the use of a sugar solution instead of water as a diluent in dark-colored products.

(4) That factors be determined for the formula used in calculating commercial glucose to replace the factors 175 and 163 now used.

(5) That Herles's solution and neutral lead acetate be adopted provisionally as clarifying agents in polarizing cane products.

INFLUENCE OF SALTS OF THE ALKALIS ON THE OPTICAL DETERMINATION OF SUCROSE.

By C. A. BROWNE and G. H. HARDIN.

In the analysis of various classes of food products—honeys, molasses, raw sugars, jams, preserves, etc.—wide discrepancies have often been noted between the determination of sucrose by the optical methods of polarization and by the gravimetric

methods of inversion. These discrepancies have been explained in part by such errors as that due to the volume of the lead precipitate, or the effect of the inverting acid upon the specific rotation of levulose, or variations in temperature of polarization. The differences are in many cases so great that none of these sources of error seems to offer a satisfactory solution. The question is one of such importance in the analysis and valuation of many sugar-containing products that it has been recently subjected by the authors to a critical study. While the results of their investigations are not as yet fully completed the work has progressed sufficiently to warrant a preliminary announcement.

The authors' investigations show that a very important factor has been neglected in the calculation of sucrose by the Clerget or Herzfeld method of double polarization, the result being that the sucrose as thus determined is often a per cent or more below the true amount in the case of low-grade products. The factor referred to is the depressing effect which soluble salts or hydroxids of the alkalis have on the specific rotation of sucrose.

It is a well-known fact that nearly all soluble salts cause a lowering of the specific rotation of sucrose. Tables illustrating this influence are given in the works of Landolt and of Lippmann. These tables all show that the salts of the strongest acids, such as sulphates and chlorids, exercise the least influence, while the salts of the weaker acids, such as acetates and carbonates, exercise the greatest influence, in depressing the polarization of sucrose. The free alkalis, however, show the strongest action in this respect, the lowering in polarization being no doubt due to the formation of soluble saccharates of lower specific rotation. Neutralization of the free alkalis with acids will restore the rotation to the point of depression caused by the corresponding amount of salt.

Neutral mixed salts of organic and inorganic acids when added to solutions of sugar in amounts corresponding to the ash content of cane and beet molasses were found by the authors to cause a depression in polarization of about 0.5 per cent. The error due to the depressing influence of salts of the alkalis becomes much intensified, however, after the addition of the basic lead solution used for clarification. Insoluble lead salts are precipitated with a liberation of free alkalis, the latter lowering the polarization of the sucrose much below its true reading.

The depressing influence of the free alkali liberated by basic lead acetate may be compensated more or less by other errors incident to the process of clarification. Among these compensating errors may be mentioned the volume-of-precipitate error and the precipitation-of-levulose error.

In the case of sugar-beet products, which are comparatively free from reducing sugars, the volume of lead precipitate will counterbalance to a considerable extent the depression in rotation of sucrose caused by the salts and hydroxids of the alkalis. If there is no volume-of-precipitate error, as in Horne's method of dry lead defecation, the depressing effect of the liberated free alkali is uncompensated and very low polarizations may result.

In the case of sugar cane and other products containing levulose the precipitation of the latter will usually more than counterbalance the error due to the depression in specific rotation of sucrose, with the result that too high polarizations are secured.

The extent to which the numerous errors involved in the optical determination of sucrose in any given product will compensate one another is always a question. A determination of sucrose or of raffinose in low-grade products by any of the customary optical methods can be regarded therefore as only an approximation; the error of ± 0.50 per cent, which is allowed by many chemists in European countries in determinations of sucrose and raffinose by optical methods, is certainly none too great.

REPORT OF COMMITTEE B ON RECOMMENDATIONS OF REFEREES.

F. W. Woll, *Chairman.*[1]

(Dairy products, foods and feeding stuffs, sugar, tannin, and medicinal plants and drugs.)

Foods and Feeding Stuffs.

It is recommended—

(1) That the referee's method for the determination of acidity in feeds be further studied (see p. 152).

This recommendation was adopted as presented by the committee (the referee having recommended the adoption of the method as provisional), together with the following, also offered by the committee on recommendations:

(2) That the subject of acidity in commercial feeds be further studied with special reference to eliminating the error due to proteids or deciding whether the acidity due to proteids should be included in the determination.

Recommendations 1 and 2 were adopted.

(3) That the referee make a study of the literature on the amount of protein in the various vegetable products used for feed and report to the association at the 1911 meeting on the advisability of adopting more accurate factors for converting nitrogen into protein than the present factor of 6.25.

Adopted.

(4) That the referee study the method of extracting fat with petroleum ether boiling below 65° C., and other solvents, as applied to cottonseed products.

Adopted.

(5) That the proposed modification of the official method for the determination of crude fiber in foods and feeding stuffs be further studied. (See paper by Mr. Sweeney, p. 158.)

Carried.

Dairy Products.

It is recommended—

(1) That the Roese-Gottlieb method be adopted as provisional for the determination of fat in milk, and condensed milk, both sweetened and unsweetened.

Carried. (Recommended to the committee by G. E. Patrick as official.)

(2) That the Roese-Gottlieb method be further studied for the analysis of ice cream, milk powders, malted milks, and milk chocolates.

Adopted.

(3) That the referee on dairy products study the determination of the modified Schmidt-Bondzynski method as presented by G. E. Patrick, for the determination of fat in cheese.

Adopted.

These methods read as follows:

THE ROESE-GOTTLIEB METHOD FOR THE DETERMINATION OF FAT IN CONDENSED AND EVAPORATED MILK.

Weigh from 4 to 5 grams of the homogeneous sample of condensed or evaporated milk into a Röhrig tube [2] or some similar apparatus and dilute with water in the tube to about 10.5 cc (or, if preferred, weigh into the tube from 10 to 11 grams of a 40 per cent solution of the substance). Add 1.25 cc of concentrated ammonium hydroxid (2 cc if the sample is sour) and mix thoroughly with the milk. Add 10 cc of 95 per cent alcohol and mix well. Then add 25 cc of washed ethyl ether and shake vigorously for half a minute, then 25 cc of petroleum ether (redistilled slowly at a temperature below 60° C. preferably), and shake again for half a minute. Let stand 20 minutes,

[1] In the absence of the chairman this report was submitted by F. P. Veitch.

[2] Zts. Nahr. Genussm., 1905, 9: 531.

or until the upper liquid is practically clear and its lower level constant. Draw off as much as possible of the ether fat solution (usually 0.5 to 0.8 cc will be left) into a weighed flask through a diminutive, quick-acting filter of selected paper. The flask should always be weighed with a similar one as counterpoise.

Reextract the liquid remaining in the tube, this time with only 15 cc of each ether, shaking vigorously half a minute with each, and allow to settle. Draw off the clear solution through the small filter into the same flask as before and wash the tip of spigot, the funnel, and the filter with a few cubic centimeters of a mixture of the two ethers in equal parts (previously mixed and free from deposited water). For absolutely exact results the reextraction must be repeated. This third extraction yields usually not more than about a milligram of fat if the previous ether-fat solutions have been drawn off closely, an amount averaging about 0.02 per cent on a 4-gram charge. Evaporate the ether slowly on the steam bath, then dry the fat in a boiling water oven until loss of weight ceases.

Prove the purity of the fat by dissolving in a little petroleum ether. Should a residue remain, wash the fat out completely with petroleum ether, dry the residue, weigh, and deduct the weight. (This should not often be necessary.) Finally deduct the weight obtained by blank determination on the chemicals used.

ROESE-GOTTLIEB METHOD FOR THE DETERMINATION OF FAT IN ICE CREAM.

Weigh from 3 to 5 grams of the homogeneous sample into a Röhrig tube or similar apparatus, dilute with water to about 10.5 cc, and proceed as in the determination of fat in condensed milk.

ROESE-GOTTLIEB METHOD FOR THE DETERMINATION OF FAT IN MILK POWDER.

Weigh 1 gram of the powder in a 30 cc lipped beaker. Rub up with 9 cc of water and 2 cc of concentrated ammonium hydroxid, digest on steam bath until the casein is well softened and the whole resembles milk. Cool, transfer to a Röhrig tube or similar apparatus, using 10 cc of 95 per cent alcohol for rinsing, followed (after shaking contents of tube) by 25 cc of washed ethyl ether. Shake vigorously for one-half minute, and proceed as in the determination of fat in condensed milk.

SCHMIDT-BONDZYNSKI METHOD, MODIFIED, FOR THE DETERMINATION OF FAT IN CHEESE.

Rub up 1 gram of the homogeneous sample with 9 cc of water and 1 cc of concentrated ammonium hydroxid in a narrow beaker of from 100 to 125 cc capacity, using a glass rod; digest at a gentle heat until the casein is well softened; neutralize[1] with concentrated hydrochlorid acid (using litmus paper as an indicator); add 10 cc of concentrated hydrochlorid acid and boil gently for five minutes, keeping the beaker covered with a watch glass and adding a pinch of sand to prevent bumping. Cool somewhat, transfer to a Röhrig tube or some similar apparatus, rinsing the beaker with 25 cc of washed ethyl ether; shake well, add 25 cc of petroleum ether of the quality used in the Roese-Gottlieb method for fat in other milk products, and proceed as in that method.

Tannin.

It is recommended—

(1) That the work be continued, paying special attention to the extraction of water solubles, determination of fats, comparison of the determination of nitrogen on the original and on the fat-free sample, and the development of tests indicative of the wearing qualities of leather.

Carried.

Medicinal Plants and Drugs.

It is recommended—

(1) That the provisional methods for the determination of alkaloids designated as "(*a*) Total extraction method," and "(*b*) Aliquot method" (see Bureau of Chemistry Bul. 107, Rev., p. 258), with the modifications introduced in 1908 (see Bul. 122, p. 130), be replaced by the modified method suggested by the referee. (See Bul. 132, p. 192, for modifications, and Cir. 52, p. 14, for full statement of the method.)

This recommendation was referred to the association from the previous year for action in 1910, but it was recommended that action be again deferred until 1911,

[1] In practice, this neutralizing has often been omitted without apparently affecting results.

in order to afford an opportunity for conference with the committee on revision of the Pharmacopœia.

(2) That the method for the separation of acetanilid, caffein, sodium bicarbonate, and sugar be made *provisional*. (N. B.—Read *official* at the meeting by error.)

This recommendation was referred to the association from the previous year for action in 1910, and was carried. (See Bul. 132, p. 197, for method.)

(3) That the method for the estimation of acetphenetidin in the presence of caffein and other agents be made the subject of further investigation (see Bul. 132, p. 198), and in addition that the method for estimating salicylic acid in the presence of boric, benzoic, cinnamic, and other acids be tested in connection with the cooperative work contemplated for the coming year. (See p. 185.)

Carried.

(4) That the methods for the analysis of medicated soft drinks be studied and criticised by the association. (See p. 190 of the referee's report.)

(5) That the method for the determination of morphin in opium and opium preparations be studied and criticized by the association (see p. 180).

Carried.

(6) That the work on microscopical and macroscopical methods and on the microchemical study of drugs be continued along the present lines.

Carried.

(7) That two additional associate referees be appointed, as follows: One on synthetic drug products, and another on methods for the determination of the essential ingredients in medicated soft drinks containing alkaloids, digestive ferments, and drug principles, exclusive of mineral waters and simple soda-fountain beverages.

Carried.

Sugar.

It is recommended—

(1) That further work be done on the Horne dry lead clarification, with the view to ascertaining whether it is advisable to adopt it as the sole official method.

(2) That a study be made of the effect of variation in polarizations due to the composition of the basic lead acetate. (See Browne, Bul. 122, p. 223.)

(3) That the moisture determination by refractometer be further studied, with special reference to the use of a sugar solution instead of water as a diluent in dark-colored products.

(4) That factors be determined for the formula used in calculating commercial glucose to replace the factors 163 and 175 now used.

(5) That Herles solution and neutral lead acetate be adopted provisionally as clarifying agents in polarizing cane products.

As this report was received too late to be considered by Committee B, the association acted only on the first four recommendations relating to future work. These were adopted, but no action was taken on recommendation 5.

REPORT ON TANNIN.

J. S. Rogers, *Referee.*

Owing to the growing importance and usefulness of leather in the agricultural industries, and to the lack of uniformity that many of the determinations in the analysis of leather show, the work this year has been confined principally to a study of some of the methods now used in leather analysis. The determinations showing the greatest variations were moisture, fat, and water-solubles (soluble solids and non-tannins). Work was planned to determine the conditions under which the most concordant results could be obtained.

Two samples of greased harness leather, one blackened and the other fair, and two samples of tanning materials, one a sumac and the other an oak bark, were sent out, with the following directions:

Directions for Leather Work, 1910.

Please make all determinations in duplicate and report all percentages on samples as received. When an option of two methods of procedure is given, state which method was followed.

MOISTURE.

Method 1.—Dry 15 grams of the ground sample in a water oven for 15 hours at a temperature of from 95° to 98° C. The sample should be placed in a glass weighing bottle about 2½ inches high and 1⅞ inches in diameter, and the cover should be put in place when the sample is removed from the oven. Or the sample may be placed in the regulation tannin dish and covered with a small watch glass when removed. Desiccate over sulphuric acid and weigh in half an hour.

Method 2 (where a vacuum oven is available).—Dry 15 grams of the sample in a tared glass weighing bottle or tannin dish with cover in a vacuum oven at from 95° to 98° C. for four hours, put cover in place, desiccate over sulphuric acid and weigh in half an hour.

Method 3 (for greased leather).—Place 50 grams of the sample in a 600 cc Erlenmeyer flask, add 350 cc of toluol. (The toluol must be saturated with water to obtain conditions corresponding to those in actual experiment. To this end add from 25 to 50 cc of water to 750 cc of toluol, place in a flask and distil. When the distillate has stood for half an hour, carefully syphon off the toluol.) Mix thoroughly with the leather, place the flask in a bath of oil or glycerin and distil. The distillation should be carried on carefully. Only a small amount of water should flow through the condenser, since a too sudden cooling of the distillate often causes a permanent cloudiness. The vessel for receiving the distillate must have a capacity of 300 to 350 cc and should consist of a glass funnel, the capacity of which is between 300 and 350 cc, sealed into a tall 10 cc graduated cylinder, graduated to 0.1 cc. Distillation should be continued until the distillate comes over perfectly clear or until at least from 275 to 300 cc have been distilled. Any drops of water adhering to the condenser, funnel, or cylinder must be swept down by a policeman. The volume of the water is then read, and the per cent calculated.

Method 4 (for greased leather after fat extraction).—The residue from the fat extraction on the sample in which water has not been determined is removed from the Soxhlet and placed in a tared weighing bottle or tannin dish. This is then dried in a water oven at from 95° to 98° C. for 15 hours, desiccated over sulphuric acid for half an hour, and weighed. The fat extracted is deducted from the original weight, and the water calculated on the residue.

FATS.

(A) Extract 15 grams of air-dry sample and (B) 15 grams of water-free sample in a Soxhlet extractor for 16 hours or until free from grease, using petroleum ether distilling between 50° and 80° C., evaporate the ether, cool in a desiccator, and weigh.

WATER EXTRACT (BUREAU OF CHEMISTRY METHOD).

Extract 15 grams of fat-free sample with water in a Soxhlet the cylinder of which is surrounded by a water bath kept at 50° C. Continue the extraction for 14 hours, and make up the extract to 1 liter. At the beginning of the extraction 300 cc of water are poured into the Soxhlet and allowed to syphon over, then the boiling is begun. At the end of one hour the flame is removed and the extract transferred to a 1-liter graduated flask, 150 cc of water are then added, and the extraction continued two hours, the extract removed, 150 cc of water added and extraction continued for three hours and extract removed. Two more extractions are made in each of which 150 cc of water are added and the extraction continued for four hours. This gives 14 hours' extraction and an extract which does not exceed 1 liter in volume. (A small piece of cotton is placed in the bottom of the Soxhlet and another on top of the leather to prevent small particles of leather from being carried over.)

SOLUBLE SOLIDS.

To 2 grams of kaolin in a beaker add 75 cc of extract, stir, let stand 15 minutes, decant, and discard as much as possible of the supernatant liquid, and again add 75 cc of the extract to the kaolin, stir and pour at once on a No. 588 folded filter. Keep the filter full and the funnel and receiving vessel covered. Reject the first 150 cc of the filtrate. Evaporate and dry the next 100 cc (which must be clear).

Conduct the evaporation and drying in flat-bottom glass dishes from 2¾ to 3 inches in diameter. Evaporate and dry for 16 hours in a combined evaporator and drier, at from 98° to 100° C. or after evaporating dry for 12 hours on the bottom shelf of a water oven at from 98° to 100° C.

NONTANNINS.

A quantity of hide powder sufficient for the number of analyses to be made shall be prepared in the following manner: Digest with 25 times its weight of water till thoroughly soaked. Add 3 per cent of chrome alum solution, agitate by either shaking or stirring occasionally for several hours, and let stand overnight, wash by squeezing through linen, continuing the washing until the water gives no precipitate with barium chlorid. Squeeze the hide, using a press if necessary, so that the wet hide will contain between 70 and 75 per cent of moisture. Use approximately 20 grams of wet hide for moisture determination. Add to 200 cc of the original extract such quantity of the wet hide as represents from 12 to 13 grams of dry hide, shake for 10 minutes in some form of mechanical shaker and squeeze immediately through linen. Add 2 grams of kaolin to the filtrate, stir and filter through a folded filter (No. 1 F Swedish recommended) of a size sufficient to hold the entire filtrate, return until clear, and evaporate 100 cc of the filtrate. The weight of the residue must be corrected for the dilution caused by the water contained in the wet hide powder.

NOTE.—In order to limit the amount of dried hide powder used, determine the moisture in the air-dry powder and calculate the quantity equal to 12.5 grams of actual dry hide powder, take any multiple of this quantity, according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing 70 to 75 per cent of water. Weigh the whole amount and divide by the multiple of the 12.5 grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc of solution. The nontannin filtrate must not give a precipitate with a 1 per cent gelatine, 10 per cent salt solution.

TANNIN.

The tannin content is shown by the difference between the soluble solids and the corrected nontannins.

WATER EXTRACT (METHOD OF A. L. C. A.).

Digest 30 grams of fat-free leather in a percolator overnight; then extract with water at 50° C. for three hours. Make the total volume of solution to 2 liters; determine the soluble solids and nontannins by the preceding methods.

DIRECTIONS FOR WORK ON TANNING MATERIALS, 1910.

EXTRACTION OF SAMPLE (A. L. C. A. METHOD).

For bark use 40 grams and for sumac use 15 grams. Extraction shall be conducted in a form of apparatus that permits the removal of the extractive solution from the influence of the sustained high temperature and shall be continued until a portion tested with gelatine salt solution fails to give a precipitate. At least 400 cc of the extractive solution should be removed and not subjected to further heating. A thin layer of cotton must be used at the top and the bottom of the extractor to prevent fine materials from passing over. After cooling to room temperature, the extract is diluted to 2 liters.

SOLUBLE SOLIDS AND NONTANNINS.

These determinations shall be carried out as for soluble solids and nontannins in directions for leather analysis just given.

ANALYTICAL RESULTS.

Owing to a lack of time, only a limited amount of work was done on the tanning materials sent out, and until more results are obtained we do not feel justified in drawing any further conclusions with regard to the methods of analysis.

It is to be regretted that more members of the association did not cooperate. The results given are those of the associate referee, Burton J. Ray, and those obtained in the Leather and Paper Laboratory, Bureau of Chemistry.

(NOTE.—The following terms are used with the meanings indicated: Original sample=the prepared sample untreated. Water-free sample=original sample dried in water oven fifteen hours. Fat-free sample=original sample extracted with petroleum ether. Water-free, fat-free sample=original sample dried and then extracted. Fat-free, water-free sample=original sample extracted and then dried.)

Moisture.

Analyst and method.	Sample No. 1.		Sample No. 2.	
	Original.	Fat-free.	Original.	Fat-free.
B. J. Ray:	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Dried in water oven 95°–98° C.; fifteen hours	6.0	6.2	4.5	.....
	6.0	6.4	4.5	.....
Average	6.0	6.3	4.50	.....
J. S. Rogers and C. F. Speh:				
Dried in water oven 95°–98° C.; fifteen hours	6.2	5.9	4.4	4.5
	6.3	6.1	4.5	4.5
	6.3	6.0	4.5	4.5
	6.3	6.0	4.5	4.6
	6.2	5.9	4.5	4.6
	6.3	.....	4.4	.....
	6.3	.....	4.5	.....
	6.3	.....	4.5	.....
	6.2	.....	4.4	.....
	6.2	.....	4.5	.....
Average	6.26	5.98	4.47	4.54
Vacuum oven four hours, at 99° C	7.4	.....	4.7	.....
	7.5	.....	4.7	.....
Average	7.45	.....	4.70	.....
Four hours at 70° C	6.2	.....	.....	.....
	6.2	.....	.....	.....
	6.2	.....	.....	.....
Average	6.20	.....	.....	.....
B. J. Ray:				
Distillation with toluol on a sample which gave 4.29 per cent when dried in a water oven.	3.2	.....	.....	.....
	3.3	.....	.....	.....
Average	3.25	.....	.....	.....
J. S. Rogers:				
Distillation with toluol on a sample which gave 3.85 per cent when dried in a water oven.	3.5	.....	.....	.....
	3.4	.....	.....	.....
Average	3.45	.....	.....	.....

Fats.

Analyst.	Sample No. 1.		Sample No. 2.	
	Original.	Water-free.	Original.	Water-free.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
B. J. Ray	9.8	9.6	8.9	8.4
	9.8	9.4	8.8	8.2
Average	9.80	9.50	8.85	8.30
Bone dry	10.42	10.10	9.26	8.69
J. S. Rogers and C. F. Speh	10.4	9.8	8.6	8.8
	10.3	9.6	9.1	8.6
	10.1	9.9	9.4	9.0
	10.0	9.7	9.2	8.9
	10.2	9.4	8.9	9.0
	10.2	.....	8.7	8.7
	10.3	.....	8.9	8.5
	10.3	.....	8.8	8.7
	10.2	.....	8.9	8.6
	10.2	.....	8.7	8.7
	.....	.....	8.8	8.6
	.....	.....	8.7	8.6
	.....	.....	8.9	8.6
	.....	.....	8.8	8.7
Average	10.22	9.68	8.88	8.71
Bone dry	10.90	10.31	9.29	9.11

Water extraction of the fat-free sample (B. J. Ray).

Data.	Bureau of Chemistry method.		A. L. C. A. method.	
	Sample 1.	Sample 2.	Sample 1.	Sample 2.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Soluble solids	9.82	26.17	8.18	23.22
	9.84	26.60	8.16	23.26
Average	9.83	26.39	8.17	23.24
Bone dry	10.45	27.63	9.25	24.33

Moisture and fat were determined on a sample of leather that had been cut in small pieces instead of being ground, and the results were both decidedly higher on the former than on the ground sample. Water that is present in the fat extracted from the leather by petroleum ether evidently can be easily removed by drying in a water oven, and has no appreciable effect on the weight of the fat residue.

To determine whether any fat volatilizes during the water determination at 98° to 100° C. in a water oven for fifteen hours, 20 grams of leather were placed in a flask in a boiling water bath and a small current of air passed over the leather. The heating was continued six hours. The portions volatilized were condensed in a long glass tube. When the fat was dissolved in ether and weighed, it gave 0.002 gram or 0.01 per cent of the original leather. This indicates that only a very small amount of fat is volatilized during water determination on the original sample.

In the preceding tables it will be noted that moisture on the original ground sample gave, as a rule, higher results than on the fat-free sample, and that the results for fats were in all cases higher on the original sample than on the water-free sample. Moisture determined by distillation with toluol gave lower results than when determined by drying in the water oven. Moisture determined in the vacuum at 70° C. for four hours gave practically the same percentages as when determined by drying in the water oven. But when the temperature was 100° C. for four hours, the loss in weight was increased about 1 per cent.

Mr. Ray calls attention to, and gives data to illustrate, the fact that when hide powder is chromed and washed ready for use and then allowed to stand in an air-tight jar, its soluble solids increase in proportion to the time it is allowed to stand before using. Twenty grams of wet hide were shaken with 200 cc of distilled water and filtered with the following results:

After 1 hour 100 cc of filtrate gave a residue of 0.0049 gram.
After 48 hours 100 cc of filtrate gave a residue of 0.0113 gram.
After 72 hours 100 cc of filtrate gave a residue of 0.0240 gram.
After 96 hours 100 cc of filtrate gave a residue of 0.0542 gram.

In the comparison of the A. L. C. A. method of extraction with that of the Bureau of Chemistry, two extractions by the former and five by the latter method were made on samples Nos. 1 and 2, using the original sample, a fat-free sample, and a water-free sample in each case. The Bureau of Chemistry method in every case gave higher soluble solids, while the nontannins by the two methods were very nearly the same. This indicates that the difference in results lies in the amount of tannin extracted. The longer and the more thorough extraction evidently brings out the more difficultly soluble tannins. The A. L. C. A. method gave approximately 3 per cent less tannin on sample No. 1, and 5 per cent less on sample No. 2, than the method of the Bureau of Chemistry. The Bureau of Chemistry method is preferred to that of the A. L. C. A. because it gives higher water solubles (evidently tannin) and, to the best of our knowledge, does not break up the leather or remove combined tannin.

In order to determine the condition of sample best adapted for water extraction, five (in two cases four) extractions were made on samples No. 1 and No. 2, using in each case the original sample, a water-free sample, a fat-free sample, a water-free fat-free sample, and a fat-free water-free sample. The results from the extraction of the samples under these different conditions vary considerably, as shown in the following tables. The fat-free sample gave in all cases the highest soluble solids and nontannins. The original sample gave the second highest results. The other extractions, as a rule, gave results much lower than either the fat-free or the original sample. The five extractions on the original were more uniform than the five on the fat-free sample. The percentages of soluble solids, nontannins, and tannins obtained on the original sample were only a little lower than those obtained on the fat-free sample. The condition of sample best adapted for water extraction seems to rest between the fat-free sample and the original. The water-free, water-free fat-free, and the fat-free water-free, all give results so low that their use can not be considered. It will be necessary to continue the work on the original and on the fat-free samples in order to determine which is to be preferred for water extraction.

Results on water extractions varying the preparation of the sample (J. S. Rogers and C. F. Speh).

[All averages in italics are calculated to the bone-dry basis.]

Sample.	Bureau of Chemistry method.						American Leather Chemists Association method.					
	Soluble solids.		Nontannins.		Tannins.		Soluble solids.		Nontannins.		Tannins.	
	Duplicates.	Averages.	Duplicates.	Averages.	Duplicates.	Averages.	Duplicates.	Averages.	Duplicates.	Averages.	Duplicates.	Averages.
Sample No. 1:												
Original—	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
1	11.03	10.90	4.02	3.96	7.01	7.04	8.34	8.30	4.75	4.60	3.59	3.75
	10.95	*11.44*	3.89	*4.20*	7.06	*7.32*	8.26	*8.63*	4.45	*4.79*	3.81	*3.84*
2	10.55	10.52	3.88	2.92	6.69	6.61	8.81	8.52	4.58	4.71	4.23	3.92
	10.49	*11.22*	3.96	*4.18*	6.53	*7.05*	8.43	*8.97*	4.83	*4.89*	3.60	*4.08*
3	10.57	10.57	3.79	3.77	6.78	6.80	.....	.....	.....	.....	.....	.....
	10.56	*11.27*	3.75	*4.02*	6.81	*7.25*	.....	.....	.....	.....	.....	.....
4	9.73	9.78	3.76	3.83	5.97	5.95	.....	.....	.....	.....	.....	.....
	9.82	*10.43*	3.89	*4.08*	5.93	*6.35*	.....	.....	.....	.....	.....	.....
5	10.40	10.41	3.80	3.82	6.60	6.59	.....	.....	.....	.....	.....	.....
	10.41	*11.10*	3.84	*4.07*	6.57	*7.03*	.....	.....	.....	.....	.....	.....
General average	.....	10.45	.....	3.86	.....	6.59	.....	8.41	.....	4.66	.....	3.84
	.....	*11.09*	.....	*4.11*	.....	*6.98*	.....	*8.80*	.....	*4.84*	.....	*3.96*
Water-free—												
1	9.05	9.08	3.46	3.53	5.59	5.55	.....	.....	.....	.....	.....	.....
	9.11	*9.68*	3.60	*3.77*	5.50	*5.92*	.....	.....	.....	.....	.....	.....
2	9.32	9.32	3.60	3.62	5.72	5.71	.....	.....	.....	.....	.....	.....
	9.32	*9.94*	3.63	*3.86*	5.69	*6.09*	.....	.....	.....	.....	.....	.....
3	9.43	9.48	3.67	3.66	5.76	5.83	.....	.....	.....	.....	.....	.....
	9.53	*10.11*	3.64	*3.90*	5.89	*6.22*	.....	.....	.....	.....	.....	.....
4	9.50	9.57	3.80	3.79	5.70	5.78	.....	.....	.....	.....	.....	.....
	9.64	*10.21*	3.78	*4.04*	5.86	*6.16*	.....	.....	.....	.....	.....	.....
5	9.49	9.49	3.72	3.56	5.75	5.92	.....	.....	.....	.....	.....	.....
	9.48	*10.11*	3.39	*3.80*	6.09	*6.31*	.....	.....	.....	.....	.....	.....
General average	.....	9.38	.....	3.63	.....	5.76	.....	.....	.....	.....	.....	.....
	.....	*10.01*	.....	*3.87*	.....	*6.14*	.....	.....	.....	.....	.....	.....
Fat-free—												
1	10.48	10.46	4.17	4.06	6.31	6.41	8.99	9.00	4.07	4.05	4.92	4.96
	10.43	*11.16*	3.94	*4.33*	6.51	*6.84*	9.01	*9.36*	4.02	*4.21*	4.99	*5.16*
2	10.63	10.81	3.95	3.95	6.68	6.86	8.47	8.47	4.63	4.60	3.84	3.88
	10.98	*11.53*	3.94	*4.21*	7.04	*7.32*	8.47	*8.81*	4.56	*4.78*	3.91	*4.03*
3	11.45	11.48	3.99	3.98	7.46	7.50	.....	.....	.....	.....	.....	.....
	11.50	*12.25*	3.97	*4.25*	7.53	*8.00*	.....	.....	.....	.....	.....	.....
4	10.90	10.96	4.18	4.07	6.72	6.90	.....	.....	.....	.....	.....	.....
	11.02	*11.69*	3.95	*4.34*	7.07	*7.36*	.....	.....	.....	.....	.....	.....
5	11.43	11.44	4.83	4.83	6.60	6.60	.....	.....	.....	.....	.....	.....
	11.44	*12.20*	.....	*5.15*	.....	*7.04*	.....	.....	.....	.....	.....	.....
General average	.....	11.03	.....	4.18	.....	6.85	.....	8.74	.....	4.33	.....	4.41
	.....	*11.76*	.....	*4.46*	.....	*7.31*	.....	*9.09*	.....	*4.50*	.....	*4.59*
Water-free, fat-free—												
1	9.08	9.19	3.52	3.54	5.56	5.65	6.19	6.20	3.28	3.31	2.91	2.89
	9.29	*9.80*	3.56	*3.78*	5.73	*6.03*	6.21	*6.45*	3.33	*3.44*	2.88	*3.02*
2	9.21	9.19	3.63	3.64	3.58	3.55	.....	.....	.....	.....	.....	.....
	9.17	*9.80*	3.65	*3.88*	5.52	*5.92*	.....	.....	.....	.....	.....	.....
3	9.51	9.47	3.54	3.54	5.97	5.93	.....	.....	.....	.....	.....	.....
	9.43	*10.10*	3.54	*3.78*	5.89	*6.32*	.....	.....	.....	.....	.....	.....
4	9.17	9.15	3.34	3.35	5.83	5.80	.....	.....	.....	.....	.....	.....
	9.12	*9.76*	3.36	*3.58*	5.76	*6.19*	.....	.....	.....	.....	.....	.....
5	9.73	9.72	3.61	3.66	6.12	6.06	.....	.....	.....	.....	.....	.....
	9.71	*10.37*	3.72	*3.90*	5.99	*6.46*	.....	.....	.....	.....	.....	.....
General average	.....	9.34	.....	3.55	.....	5.80	.....	6.20	.....	3.31	.....	2.89
	.....	*9.97*	.....	*3.78*	.....	*6.19*	.....	*6.45*	.....	*3.44*	.....	*3.02*

Results on water extractions varying the preparation of the sample (J. S. Rogers and C. F. Speh)—Continued.

Sample.	Bureau of Chemistry method.						American Leather Chemists Association method.					
	Soluble solids.		Nontannins.		Tannins.		Soluble solids.		Nontannins.		Tannins.	
	Duplicates.	Averages.	Duplicates.	Averages.	Duplicates.	Averages.	Duplicates.	Averages.	Duplicates.	Averages.	Duplicates.	Averages.
Sample No. 1—Continued.												
Fat-free, water-free—	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
1	6.86	6.84	3.12	3.05	3.74	3.80						
	6.82	*7.30*	2.97	*3.25*	3.85	*4.05*						
2	6.99	7.01	3.02	3.00	3.97	4.01						
	7.03	*7.48*	2.99	*3.20*	4.04	*4.23*						
3	7.48	7.49	3.10	3.15	4.38	4.34						
	7.49	*8.00*	3.19	*3.36*	4.30	*4.63*						
4	5.59	5.67	2.52	2.53	3.07	3.14						
	5.74	*6.05*	2.53	*2.70*	3.21	*3.35*						
General average		6.75		2.93		3.82						
		7.21		*3.13*		*4.08*						
Sample No. 2:												
Original—												
1	27.01	27.01	18.62	18.56	8.39	8.44	25.27	25.30	19.25	19.34	6.02	5.96
	27.00	*28.25*	18.51	*19.41*	8.49	*8.83*	25.32	*26.44*	19.42	*20.21*	5.90	*6.23*
2	27.71	27.71	19.32	19.27	8.39	8.44	24.83	24.85	20.01	19.90	4.82	4.95
	27.70	*28.99*	19.22	*20.16*	8.48	*8.83*	24.86	*25.97*	19.78	*20.79*	5.08	*5.18*
3	26.63	26.59	18.63	18.68	8.00	7.91						
	26.55	*27.81*	18.73	*19.54*	7.82	*8.37*						
4	27.27	27.14	18.69	18.87	8.58	8.27						
	27.00	*28.39*	19.04	*19.74*	7.96	*8.65*						
5	26.97	27.07	19.32	19.11	7.65	7.96						
	27.19	*28.31*	18.90	*20.00*	8.27	*8.43*						
General average		27.10		18.90		8.20		25.08		19.62		5.46
		28.35		*19.77*		*8.58*		*26.21*		*20.49*		*5.72*
Water-free—												
1	25.09	25.08	16.81	17.09	8.28	8.00						
	25.07	*26.23*	17.36	*17.88*	7.71	*8.37*						
2	24.70	24.63	17.43	17.26	7.27	7.39						
	24.55	*25.76*	17.07	*18.05*	7.48	*7.73*						
3	23.83	23.85	17.21	17.09	6.62	6.76						
	23.86	*24.95*	16.96	*17.88*	6.90	*7.07*						
4	24.64	24.64	17.11	17.20	7.53	7.44						
	24.63	*25.77*	17.29	*17.99*	7.34	*7.78*						
General average		24.55		17.16		7.39						
		25.68		*17.95*		*7.73*						
Fat-free—												
1	28.30	28.35	18.27	18.17	10.03	10.18	24.14	24.09	19.13	19.14	5.01	4.95
	28.39	*29.65*	18.07	*19.01*	10.32	*10.65*	24.04	*25.19*	19.14	*20.00*	4.90	*5.17*
2	27.39	27.47	18.91	18.93	8.48	8.54	24.42	24.39	19.28	19.26	5.14	5.13
	27.54	*28.73*	18.95	*19.80*	8.59	*8.93*	24.36	*25.49*	19.24	*20.13*	5.12	*5.36*
3	28.39	28.40	18.95	18.92	9.44	9.48						
	28.41	*29.70*	18.89	*19.78*	9.52	*9.91*						
4	28.58	28.60	19.28	19.25	9.30	9.35						
	28.61	*29.90*	19.22	*20.14*	9.39	*9.78*						
5	28.78	28.77	19.30	19.21	9.48	9.57						
	28.76	*30.09*	19.11	*20.09*	9.65	*10.01*						
General average		28.32		18.89		9.42		24.24		19.20		5.04
		29.62		*19.76*		*9.85*		*25.34*		*20.07*		*5.27*
Water-free, fat-free—												
1	25.33	25.31	17.17	17.15	8.16	8.16	19.17	19.15	15.41	15.41	3.76	3.76
	25.28	*26.47*	17.13	*17.94*	8.15	*8.53*	19.13	*20.01*		*16.10*		*3.93*
2	26.09	26.09	17.17	17.18	8.92	8.92	20.47	20.42	16.61	16.73	3.86	3.69
	26.09	*27.29*	17.18	*17.98*	8.91	*9.33*	20.26	*21.34*	16.84	*17.44*	3.52	*3.86*
3	25.76	25.71	17.26	17.36	8.50	8.35						
	25.66	*26.89*	17.46	*18.16*	8.20	*8.73*						
4	25.91	25.90	17.20	17.25	8.71	8.65						
	25.88	*27.09*	17.30	*18.04*	8.58	*9.05*						
5	25.99	26.02	17.39	17.42	8.60	8.61						
	26.04	*27.22*	17.43	*18.22*	8.61	*9.01*						
General average		25.81		17.27		8.54		19.79		16.07		3.72
		26.99		*18.06*		*8.93*		*20.68*		*16.78*		*3.90*

Results on water extractions varying the preparation of the sample (J. S. Rogers and C. F. Speh)—Continued.

Sample.	Bureau of Chemistry method.						American Leather Chemists Association method.					
	Soluble solids.		Nontannins.		Tannins.		Soluble solids.		Nontannins.		Tannins.	
	Duplicates.	Averages.	Duplicates.	Averages.	Duplicates.	Averages.	Duplicates.	Averages.	Duplicates.	Averages.	Duplicates.	Averages.
Sample No. 2—Continued.												
Fat-free, water-free—	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*						
1	26.00	25.98	17.28	17.37	8.72	8.62	.....	.....	.....	.....	.....	.....
	25.96	*27.17*	17.45	*18.17*	8.51	*9.02*	.....	.....	.....	.....	.....	.....
2	25.27	25.32	17.20	17.08	8.07	8.24	.....	.....	.....	.....	.....	.....
	25.37	*26.48*	16.96	*17.87*	8.41	*8.62*	.....	.....	.....	.....	.....	.....
3	26.43	26.39	17.35	17.41	9.08	8.99	.....	.....	.....	.....	.....	.....
	26.35	*27.60*	17.46	*18.21*	8.89	*9.40*	.....	.....	.....	.....	.....	.....
4	25.87	25.87	17.06	17.02	8.81	8.86	.....	.....	.....	.....	.....	.....
	25.87	*27.06*	16.97	*17.80*	8.90	*9.27*	.....	.....	.....	.....	.....	.....
5	26.57	26.54	17.44	17.44	9.13	9.10	.....	.....	.....	.....	.....	.....
	26.50	*27.76*	17.43	*18.24*	9.07	*9.52*	.....	.....	.....	.....	.....	.....
General average	.....	26.02	.....	17.26	.....	8.76	.....	.....	.....	.....	.....	.....
	.....	*27.22*	.....	*18.05*	.....	*9.16*	.....	.....	.....	.....	.....	.....

Conclusions.

(1) Moisture should be determined on the carefully ground original sample, which has been allowed to come to an air-dry condition after grinding.

(2) Fats should be determined on the prepared original sample.

(3) Water extraction should be made by the Bureau of Chemistry method, and until further investigation shows that the fat-free sample is to be preferred, the referee recommends the use of the original sample for the extraction of water solubles.

(4) It is recommended that the work be continued, paying special attention to the extraction of water-solubles, determination of fats, comparison of the determination of nitrogen on the original sample and on the fat-free sample, and the development of tests indicative of the wearing qualities of leather.

REPORT OF COMMITTEE ON COMPILATION OF BY-LAWS.

Mr. Bigelow, on behalf of the committee on the compilation of by-laws (Messrs. C. L. Penny and R. N. Brackett, members), made a final report after consultation with the committee on amendments to the constitution. The report was discussed at some length and was adopted, the committee being authorized to make such changes as were necessary to embody the fact that the dues were not to be cumulative. It was also brought out that the agricultural colleges and the experiment stations were considered as separate units. The by-laws as adopted are to be found on page 202, following the constitution.

The meeting adjourned until the afternoon session.

SATURDAY—AFTERNOON SESSION.

PLATINUM LABORATORY UTENSILS.

By Percy H. Walker and F. W. Smither.

In Roscoe and Schorlemmer's Treatise on Chemistry,[1] it is stated that "in order to test whether a new platinum crucible be of proper quality, it is first boiled with hydrochloric acid and afterwards with pure nitric acid. If none of the metal be dissolved the platinum is good." Until within the last few years this statement has been considered correct, and samples which could be heated to bright redness for a very few minutes and subjected to the above test without showing any change were accepted as good. In the spring of 1908 a number of platinum crucibles were bought, tested as described, accepted, and used along with older crucibles for general analytical work. It was noticed that these crucibles were quite hard and stiff and very hard to keep clean. Within a few months several of them developed cracks, and after prolonged heating they were stained, and in cleaning iron was frequently found. In addition to the discoloration caused by heating the crucibles, their weight did not remain constant. Of course, the possibility of contamination by substances heated in it made it impossible to say positively, after using a crucible for several months, that it was originally faulty, but the fact that there was trouble with all of this shipment and comparatively little trouble from the old soft crucibles made it highly probable that the fault was with the crucibles when received.

Some time later a new crucible was heated over a blast lamp and a very slight reddish film found on the inside. The crucible was returned to the maker and replaced, no attempt being made to find out what the deposit was, since it was desired that the manufacturer see it. At about this time W. F. Hillebrand stated that he had found iron in new platinum crucibles and suggested that the reddish film observed was iron. An inquiry among a number of chemists in the Bureau of Chemistry developed the fact that most chemists have favorite platinum vessels, which they prefer to others. Most of these favorite pieces which are easily kept clean and undergo very little change in weight are soft.

Last August a large order, amounting to over $3,000, was received at the Bureau of Chemistry, which proved to be practically worthless for laboratory use and had to be rejected. If this ware had been subjected only to the tests described by Roscoe and Schorlemmer, it would probably have been accepted; but on prolonged heating all of the pieces tested developed a reddish film, which dissolved in hot hydrochloric acid and gave a strong iron reaction On prolonged heating the loss in weight was excessive. For example, a Gooch crucible with cap and lid (No. 370), after being heated to redness and cooled, weighed 31.4911 grams. After heating over a blast lamp for four hours, the weight was 31.4858, a loss in weight of 4.3 milligrams. The whole surface was covered with a reddish film, that on the under side of the lid being almost black and not easily removed. The coating on the under side of the lid was observed with several crucibles and it was proved to contain iron by fusing with potassium hydrogen sulphate and testing the fusion On heating such a deposit in a reducing flame it becomes much lighter in color (gray), but the dark color can be brought back in part by heating in the oxidizing flame. This coating is probably magnetic oxid (Fe_3O_4).

Another dish (No. 1065) which, after heating and cooling, weighed 22.5600 grams, after heating for two hours in an electric muffle at a temperature of about 1075° C., weighed 22.5594 grams. The dish showed the characteristic reddish film. It was

[1] 4th ed., v. 2, p. 1357.

put in a porcelain dish with strong hydrochloric acid, covered, and heated on the steam bath for about two hours, removed from the acid, washed, heated to redness, cooled, and weighed. This weight was 22.5460 grams, a total loss of 14 milligrams. When the hydrochloric acid solution was evaporated to about 5 cc and iron determined colorimetrically, 6.1 milligrams of iron were found.

The manufacturer of this platinum insisted at first that the ware was all right, and it was only after a demonstration, in comparison with a good crucible, that he became convinced that it was not unreasonable to reject the ware. In order to convince contractors who might be inclined to insist that the old crucibles had not been originally resistant to reagents and heat and that the ware had been purified by years of use in the laboratory, two crucibles were purchased from a foreign manufacturer, which were guaranteed to be absolutely pure platinum. These were heated, cooled, and weighed; then heated over the blast lamp for two hours, digested with strong hydrochloric acid on steam bath for two hours, washed, ignited, cooled, and weighed, with the following results:

Effects of tests on pure platinum.

Crucible number.	Original weight.	Weight after blasting.	Final weight.
	Grams.	*Grams.*	*Grams.*
394	18.0856	18.0855	18.0855
365	17.9885	18.9884	17.9884

These crucibles remained perfectly bright during the whole operation. From the undoubted fact that some platinum ware on the market is absolutely unfitted for laboratory use, and that a very large proportion of it is of doubtful quality, great care should be exercised in testing carefully each piece, and if possible a standard specification should be adopted. As a basis for forming a satisfactory specification, we would suggest the following:

The platinum for crucibles, dishes, and other laboratory apparatus should be pure platinum. Do not accept the so-called hard platinum. Heat each article to redness, cool, and weigh; then heat for not less than four hours with a blast lamp, or in a muffle at a temperature of not less than 1000° C. (1200° C. is better). If, after this treatment, the metal shows any tarnish or darkening on the inner surface, reject it without further test. If no tarnish appears on the metal, digest with pure strong hydrochloric acid on the steam bath for one hour, wash, ignite, cool, and weigh. Reheat for one hour over blast or in muffle and digest with pure, strong nitric acid for one hour on steam bath, wash, ignite, cool, and weigh. Any appreciable change in weight or any evidence of anything going into solution in the acids used will be cause for rejection. The purchaser reserves the right to apply any additional tests.

REPORT ON MEDICINAL PLANTS AND DRUGS.

By G. W. Hoover.[1]

In regard to the status of drug assaying it may be said that during the past few years it has been found necessary to apply the pharmacopœial and other methods of analysis to commodities imported into the United States and subject to interstate commerce. In many instances the samples under investigation represented transactions of considerable magnitude. Importers and dealers did not as a rule accept some of the findings without protest and verification. So far, however, the results have stood the test. Only a single instance is recalled where there was a material difference in the findings, although it is almost always necessary to allow for certain

[1] In the absence of the referee, Mr. Kebler, Mr. Hoover submitted the report in his behalf.

variations. On the whole, however, the results obtained by the present pharmacopœial methods for determining the various alkaloidal constituents present in potent drugs are fairly satisfactory, considering all of the disturbing factors encountered. The question naturally arises as to the permissible variation in analytical work of this character. It is impossible to draw a sharp line of demarcation for any commodity, and it is always necessary to take into consideration the nature of the article, its characteristics, and other factors that may arise.

During the past six years the Association of Official Agricultural Chemists has, through a referee, continued a series of cooperative investigations along certain lines. These results have been published in the proceedings of the association and serve as a basis for arriving at the reasonable variations obtained by workers conducting their analyses in different sections of the country. It is a well-known fact that two or more chemists working side by side or under the same management obtain more concordant and uniform results than those working apart from one another.

In order to arrive at some conclusion as to the variation that should be permitted on results obtained by various workers on different commodities, the cooperative results obtained and published since the year 1906 have been carefully studied.

A review of the work done by the association shows a variation for opium between 5 per cent and 10 per cent based on the amount present as 100 per cent. In the case of cinchona, the variation is 15 per cent, and ipecac and nux vomica 10 per cent; the variation for aconite leaves by the pharmacopœial method is 25 per cent; for the same drug by another method, 7.5 per cent; aconite root 20 per cent by the pharmacopœial method and 25 per cent by another method based on aliquot parts; belladonna leaves by the pharmacopœial method, 20 per cent; by another method based on an aliquot, 10 per cent; belladonna root, by pharmacopœial method, 15 per cent; by a second method based on an aliquot, 5 per cent. In the case of cinchona (yellow) by the same table the variation for total alkaloids by the pharmacopœial method was less than 1 per cent. The ether soluble alkaloid, however, by the same method is 15 per cent; the total alkaloids determined by a second method varied slightly over 10 per cent, whereas the ether soluble alkaloidal variation was less than 1 per cent. In the case of red cinchona the results are about the same as for yellow cinchona; coca leaves, variation by both methods, is approximately 25 per cent; colchicum corm, pharmacopœial method, varies nearly 25 per cent; determinations made by a second method shows a variation of less than 7.5 per cent. In the case of colchicum seed the variation for the pharmacopœial method was slightly less than 25 per cent, but the variation by a second method was over 50 per cent.

A great deal of work has been done toward arriving at satisfactory methods for the determination quantitatively of morphin in various complex drug products, such as soothing sirups, drug-addiction treatments, Chinese pills and tablets, and other medicinal agents. It has been found necessary in many instances to separate morphin quantitatively in preparations containing large amounts of sugar and glycerin. All known methods which have been employed for the determination of morphin quantitatively have been tried. The shake-out method with chloroform-alcohol, as proposed by several workers, has been modified so that it gives satisfactory results.

Another subject which has demanded considerable attention is the examination of medicated soft drinks. A large number of samples of these products containing alkaloids and the active principles of drugs have been analyzed during the past three years and it has been found necessary to evolve new methods for the determination of certain of the essential ingredients and to modify the methods for other determinations in order that they might be applicable to this class of products.

H. H. Rusby, associate referee on medicinal plants, has made a careful study of the physical standards of the Pharmacopœia at the port of New York during the past few

years, and his investigation has led to the conclusions that the language employed in stating the physical standards should be far more specific and definite than it is now. On the other hand there is grave doubt as to there being good and sufficient reasons for some of the present requirements, the observance of which involves commercial inconvenience and economic loss. The settling of these doubts requires extensive pharmacological and therapeutical study as well as other investigation. Pending such investigations no changes can safely be made.

The work under the direction of W. O. Emery relating to methods for the analysis of mixtures of acetanilid, acetphenetidin, caffein, and other ingredients has been continued and extended, and Mr. Emery will report on this subject.

REPORT ON HEADACHE MIXTURES.

By W. O. Emery, *for Referee on Drugs.*

The necessity of having reliable methods, whether of general or limited utility, as a basis for investigating drugs and medicinal preparations requires no argument. In view of their widely varying composition and not infrequently highly complex nature, any analytical scheme designed for their examination should be as general in scope as possible, comprehending at the same time precise directions for the estimation of well-defined constituents possessing recognized therapeutic value. There are large classes of remedies intended for the alleviation or cure of headache, colds, grippe, rheumatism, etc., which have as their more important therapeutic agents one or several well-defined synthetic drugs, such as caffein, acetanilid, acetphenetidin, antipyrin, pyramidon, salicylates, etc., usually combined with other materials, such as sugar starch, inorganic salts, organic extracts or tissues in the case of powders, and in addition alcohol, glycerin, etc., in the case of liquids.

Of the so-called headache, cold, and grippe cures, alone, there are known to the trade no less than 800 different brands. Hence, in undertaking an investigation of this class of preparations, many of which are highly complex in nature, it early became necessary to elaborate a scheme for isolating certain well-defined constituents from the mixtures in order to estimate them quantitatively by means of specific reactions. The original procedure that had proved most satisfactory to the Bureau of Chemistry workers, and has since with slight modifications to suit special cases been tested by them on some 400 different brands, was two years ago for the first time placed in the hands of the chemists who had expressed a willingness to cooperate. Some powder mixtures were prepared and sent out with the analytical directions. The results obtained and reported at the last Washington meeting were very gratifying in view of the fact that the collaborators were operating in a comparatively new field. It was demonstrated that the method lent itself well to the quantitative separation of acetanilid, caffein, and sodium bicarbonate occurring in simple mixtures. Accordingly, further study was recommended, and at the Denver meeting the experience acquired in such work was reported. As a result a recommendation was passed to make the method, relating to mixtures involving acetanilid, caffein, and sodium bicarbonate, provisional, and to subject that relating to acetphenetidin, caffein, and sodium bicarbonate to additional study. In harmony with these recommendations, new and more complex mixtures, more nearly resembling the market brands, were prepared and examined during the past year. Unfortunately only three collaborators outside of the referee's laboratory were able to submit their results in time for incorporation in the present report. The results are as follows:

Comparative results on acetanilid mixtures.

[Percentage data.]

Analyst.	No. 4.					No. 5.				
	Chloroform-insoluble residue.	Caffein.	Acetanilid.	Sodium bicarbonate.	Celery seed.	Chloroform insoluble residue.	Caffein.	Acetanilid.	Sodium bicarbonate.	Celery seed and ginger.
F. F. Flanders, Seattle, Wash.	.....	9.13	58.19	22.96	.....	.....	9.13	58.19	22.96	.....
	.....	9.23	57.91	22.93	.....	.....	9.26	58.19	22.96	.....
C. W. Johnson,[1] Seattle, Wash.	.....	9.76	58.51	23.92	.....	.....	9.16	58.51	22.97	.....
C. C. LeFebvre, Washington, D. C.	30.02	8.88	58.03	.....	.....	31.18	9.46	58.49	.....	.....
	29.89	10.45	58.22	.....	.....	31.31	9.42	58.31	.....	.....
	30.41	9.48	58.08	.....	.....	.....	.....	.....	.....	.....
C. B. Morrison,[2] New Haven, Conn.	31.63	10.00	58.50	22.25	.....	32.80	9.63	58.50	22.94	.....
R. R. Shively, Washington, D. C.	30.31	9.40	58.12	.....	.....	31.25	9.43	58.23	.....	.....
	30.29	9.35	58.07	.....	.....	31.23	9.36	58.25	.....	.....
	30.24	9.34	58.17	.....	.....	31.07	9.43	58.25	.....	.....
W. O. Emery, Washington, D. C.	30.33	9.23	58.00	.....	.....	31.33	9.27	58.27	.....	.....
	30.28	9.22	58.10	.....	.....	31.23	9.23	58.27	.....	.....
Average	.....	9.46	58.16	23.01	.....	.....	9.34	58.31	22.96	.....
Maximum	.....	10.45	58.51	23.92	.....	.....	9.63	58.51	22.97	.....
Minimum	.....	8.88	57.91	22.25	.....	.....	9.13	58.19	22.94	.....
Difference	.....	1.57	.60	1.67	.....	.....	.50	.32	.03	.....
Known composition of mixture	.....	9.07	58.68	22.54	9.71	.....	9.07	58.68	22.54	9.71

[1] Part of work done by J. J. Wintler.

[2] Reported by J. P. Street.

As shown by the tabulated data, the findings in the case of the acetanilid mixtures are very satisfactory, particularly on No. 5, where the averages differ to a slight degree only, from the theory. A knowledge of the amount of chloroform-insoluble residue is valuable in that it affords a check on the accuracy of the caffein and acetanilid determinations. The manipulations with the tared filter give satisfactory results only when the atmospheric condition is taken into account at each weighing. In all this work on headache mixtures the second weight of a tared filter is not taken until the hygrometer shows the same moisture content or a difference not exceeding 5 per cent as compared with that observed at the first weighing.

Cooperative results on acetphenetidin mixtures.

[Percentage data.]

Analyst.	No. 6.				No. 7.					
	Caffein.	Acetphenetidin.	Sodium bicarbonate.	Citric acid.	Chloroform insoluble residue.	Caffein.	Acetphenetidin.	Sodium bicarbonate.	Guarana.	Cinnamon.
F. F. Flanders, Seattle, Wash.	8.00	58.86	23.52	.....	.....	0.20	52.66	12.60	.....	.....
		59.73	22.60	.....	.....	.23	52.90	12.88	.....	.....
C. W. Johnson,[1] Seattle, Wash.	9.63	59.90	23.45	.....	.....	.....	54.22	13.76	.....	.....
C. C. LeFebvre, Washington, D. C.	9.13	58.58	.....	.....	.....	.....	.....	.....	.....	.....
	8.68	59.05	.....	.....	.....	.....	.....	.....	.....	.....
	9.19	58.56	.....	.....	.....	.....	.....	.....	.....	.....
C. B. Morrison,[2] New Haven, Conn.	8.80	58.87	22.66	.....	46.57	.....	52.77	13.91	.....	.....
R. R. Shively, Washington, D. C.	8.83	59.87	.....	.....	45.02	.76	53.26	.....	.....	.....
	8.87	59.85	.....	.....	44.85	.82	53.30	.....	.....	.....
	9.06	59.89	.....	.....	44.94	.77	53.41	.....	.....	.....
W. O. Emery, Washington, D. C.	8.60	60.23	.....	.....	44.90	.40	53.27	.....	.....	.....
	8.77	59.90	.....	.....	44.80	.37	53.43	.....	.....	.....
Average	8.88	59.44	23.06	.....	.....	.....	53.45	13.29	.....	.....
Maximum	9.63	60.23	23.52	.....	.....	.82	54.22	13.91	.....	.....
Minimum	8.00	58.56	22.60	.....	.....	.20	52.66	12.60	.....	.....
Difference	1.63	1.67	.92	.....	.....	.62	1.56	1.31	.....	.....
Known composition of mixture	8.07	58.06	25.81	8.07	.....	.....	53.33	13.33	26.67	6.67

[1] Part of work done by J. J. Wintler. [2] Reported by J. P. Street.

The results reported on the acetphenetidin mixtures are much less uniform than those obtained with acetanilid, and indicate the necessity for further study. The real difficulty appears to hinge on the treatment of acetphenetidin with dilute sulphuric acid; 10 cc of this reagent are required by the method, and the heating on the steam bath should cease after one half, or, at the most, two-thirds, of the liquid has evaporated. If the evaporation is continued beyond this point, difficultly soluble condensation products or sulphates of phenetidin, or perhaps a mixture of both, are apparently formed, which resist acetylization and affect, accordingly, the accuracy of the method. Experiments are now under way to determine the nature of the secondary reactions observed.

In connection with work on headache and other mixtures the problem has arisen on several occasions of determining the quantity of salicylic acid present as such or in the form of its salt in preparations containing in addition one or all of the following agents: Boracic, benzoic, and cinnamic acids. It was found that the method of Bougault as applied to salicylic acid in the presence of benzoic and cinnamic acids could be used in principle; the modifications and details of procedure necessary are comprehended in the following outline:

The sample for analysis should contain about 0.1 to 0.2 gram of salicylic acid. Dissolve this sample in 100 cc of water contained in an erlenmeyer, to which has been added from 1 to 2 grams of anhydrous sodium carbonate (the amount of carbonate taken being ten times that of the salicylic acid). Heat solution nearly to boiling, then add about 35 to 70 cc of fifth-normal iodin in potassium iodid (or double this amount of tenth-normal iodin solution), enough to insure an excess of iodin. Heat one hour on steam bath to near the boiling temperature, during the course of which a violet-red precipitate of tetra-iododiphenylen-quinon $(C_6H_2I_2O)_2$ will appear. After removing the excess of iodin by the addition of a few drops of hypo, pour off the liquid through a tared Gooch crucible, taking care that most of the precipitate remains in the flask. Add 50 cc of boiling water to the precipitate in the flask, allow to digest for 10 minutes on a steam bath, then pour into the gooch, into which the precipitate is gradually washed, using for this purpose and subsequent washing

about 200 cc of hot water. Dry to constant weight in an air bath at 100° C. Multiply the weight of precipitate obtained by 0.4012 and the product will be the weight of the salicylic acid present.

The other acids present in the original mixture will be found in the filtrate from the precipitate just weighed and may be estimated according to any of several known methods.

A note on the chemical examination of American wormseed oil was presented by E. K. Nelson, which, together with additional details, will be found in Circular 73 of the Bureau of Chemistry, entitled "A Chemical Investigation of the Oil of Chenopodium."

QUANTITATIVE DETERMINATION OF KETONES IN ESSENTIAL OILS.

By E. K. Nelson.

While general methods are known for the estimation of alcohols, esters, phenols, and aldehydes in oils, such a method seems to be wanting in the case of ketones. Some substances of this class—as for example, camphor—do not react with sodium bisulphite. Others, while they may react with bisulphite, can not be even approximately estimated by its use.

The methods of Sadtler [1] and Labbé,[2] while valuable in many cases, could not be accepted as general methods because the reactions involved are not characteristic of all ketones; those usually found in essential oils, however, do react with hydroxylamin to form oxims. The method of Walther,[3] depending upon the transformation of the ketone into oxim on boiling with a standard alcoholic solution of hydroxylamin hydrochlorid in the presence of alkali, and the determination of the amount of the reagent thus consumed by titration of the excess on completion of the reaction, seemed to offer advantages as a general method for the analysis of ketone-bearing oils. Walther experimented on the estimation of citral and carvone, but does not speak of having tried the method on other ketones, or aldehydes. The following work was undertaken to test the accuracy of Walther's method on ketones in general; those used were prepared from the oils in which they occur, or were obtained on the market and purified. In every case the method was carried out in the same way. The standard hydroxylamin solution was prepared by dissolving 20 grams of hydroxylamin hydrochlorid in 30 cc of water and adding 125 cc of aldehyde-free alcohol. One to two grams of the substance were boiled under a reflux with 35 cc of this reagent and 2 grams of sodium bicarbonate, cooled, 6 cc of hydrochloric acid added, through the condenser, followed by water, and the mixture made up to 500 cc. The solution was filtered and in an aliquot part of the filtrate the free acid was neutralized by running in half-normal sodium hydroxid, using methyl orange. Phenolphthalein was then added, and the hydroxylamin left in excess of that required to form oxim was titrated with tenth-normal sodium hydroxid. The following results were obtained:

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[1] Amer. J. Pharm. 1904, **76**: 84; J. Soc. Chem. Ind. 1904, **23**: 303.

[2] Bull. soc. chim. Par., 1900, 3d ser., **23**: 283.

[3] Pharm. Zentralh. 1900, **41**: 613.

Analysis of ketones by Walther's method.

Ketone (or aldehyde).	Weight of substance.	Tenth-normal sodium hydroxid required by—		Time of boiling.	Amount of substance returned.
		35 cc of reagent.	Excess of reagent.		
	Grams.	*cc.*	*cc.*	*Hours.*	*Per cent.*
Carvone	2.3508	605.5	455.5	0.5	96.18
Do	2.3343	605.5	454.5	1.0	97.51
Do	2.2819	605.5	455.0	1.0	99.41
Do	1.9493	607.8	479.5	.5	99.12
Pulegone	2.2852	605.5	452.5	.5	101.77
Do	2.3228	605.5	451.5	1.0	100.77
Camphor	1.0250	.....	.....	.5	92.30
Do	1.0626	.....	.....	1.0	97.13
Do	2.0509	.....	.....	2.0	99.08
Do	1.7177	.....	.....	2.0	101.50
Thujone	2.2793	604.6	459.0	.5	97.10
Do	2.2903	604.6	458.0	1.0	97.30
Menthone	2.1416	.....	.....	1.0	97.50
Fenchone	.9026	578.2	527.3	2.0	85.70
Do	1.1823	578.2	540.6	1.0	50.60
Benzaldehyde	2.5447	606.7	375.0	.5	96.50
Do	2.5278	606.7	376.0	1.0	96.70

Considering the nature of the work and the difficulty of preparing absolutely pure materials to start with, these results may be considered as fairly satisfactory except in the case of fenchone. As this is a rather rare ketone, however, and as it is present in but few oils and in those only in small amount, a method for its estimation is not so necessary.

In the case of spearmint oil the Walther method was tried in comparison with the estimation of the carvone by absorption in boiling sodium hydrogen sulphite solution as well as by the Labbé method.

Results on carvone in spearmint oil.

Sample.	Labbé method.	Walther method.	Absorption in boiling.
	Per cent.	*Per cent.*	*Per cent.*
1	54.7	58.4	55.0
	.....	53.1	.....
2	61.3	65.5	67.5
	.....	66.4	.....
3	.....	61.43	61.5
	.....	60.7	.....

A sample of tansy oil, assayed by the Walther method, gave thujone 68.56 and 65.42 per cent. A sample of wormwood oil gave thujone 33.15 and 31.24 per cent. Pennyroyal oil gave 81.87 per cent of ketone by this method, calculated as pulegone ($C_{10}H_{16}O$). A mixture of pulegone with at least two other ketones is present in pennyroyal oil. A sample of rosemary oil gave 30.33 and 30.24 per cent of ketone, calculated as camphor.

The Walther method can not be recommended for the assay of any particular ketone-bearing oil until the influence on the reagent of other substances in the oil has been determined by working on known mixtures and comparison, when possible, with other methods. This work will require time. For the present it seems that the assay of oils in which carvone, camphor, pulegone or thujone is the main constituent can be made with fair accuracy by this method, affording at least a criterion of their purity.

A paper on the "Physical Standards of the Pharmacopœia," by H. H. Rusby, was read, and will be found in full in the Druggists Circular, 1910, 54 (12): 616.

NOTE ON LOBELIA SEED.

By A. G. Murray.

Of several samples of lobelia seed recently examined, a considerable proportion was found to contain excessive quantities of sand. One sample yielded more than 30 per cent of insoluble ash. There was no evidence that sand was purposely added in any of the samples, but the seed was not properly cleaned before being marketed. The plant is often not more than 8 or 10 inches high, and especially when gathered in a sandy region much sand is apt to be gathered with the seed.

In order to get some idea of the condition in which the seed comes originally into market, a sample of sifted lobelia seed was obtained from a firm of collectors in North Carolina. A portion of this was submitted to the seed laboratory of the Bureau of Plant Industry for a cleaning test. It was separated by means of a wind separator into three portions—chaff, sand, and seed. The separated sand amounted to 10 per cent. The cleaned seed yielded an ash of 12 per cent, as compared with 21 per cent for the sample as received. Some of the samples examined were satisfactory as regards the ash percentage. Four yielded ashes of approximately 10 per cent; more than 20 per cent of ash is not regarded as justifiable.

A SIMPLIFIED EXTRACTION METHOD FOR THE DETERMINATION OF MORPHIN IN OPIUM AND OPIUM PREPARATIONS.

By E. O. Eaton.

The quantitative estimation of morphin in opium and opium preparations presents many difficulties. The morphin must be separated from other opium alkaloids, which number about 20. The usual methods include precipitation and weighing of free morphin. Its limited solubility permits the recovery of about 97 per cent of the total by the U. S. P. method. Shaking-out processes with amyl alcohol, acetic ether, cresol and amyl alcohol mixtures, as proposed by several, are not satisfactory on account of the nature of the solvents. Chloroform-alcohol mixtures have been used quite successfully by several chemists. Gordin and Prescott's improved method is probably the best of those employing this solvent. Kippenberger [1] attempted to shake out morphin from a sodium hydrate and sodium bicarbonate solution. F. Wirthle [2] and W. A. Puckner [3] proved that morphin can be extracted quantitatively from solutions faintly alkaline with ammonia by chloroform-alcohol mixtures.

The weighing of an insoluble salt of morphin necessitates its being pure, in which case it can as well be titrated. The reduction of ammoniacal silver solution by morphin proved not to be quantitative. Colorimetric methods with ferricyanid and with formaldehyde, both based on its reducing properties, and with ferric chlorid, based on its phenol reaction, require the morphin to be free from interfering substances.

A limewater extraction was combined with an alcohol-chloroform shake-out in which the morphin was freed in the presence of alcohol and shaken out with chloroform. Quantitative results were obtained on a sample of the cooperative opium, which was assayed by a number of workers for data for the U. S. P. revision committee,

[1] Zts. anal. Chem. 1900, 39: 290.
[2] Chem. Ztg. 1901, 25 (1): 291.
[3] J. Amer. Chem. Soc., 1901, 23: 470–73.

average U. S. P. assay (10.77 per cent morphin); 11.20 per cent, 11 per cent, and 11.05 per cent were found by the following method:

For opium.—Dry and powder sample; place 1 gram in a 100 cc Erlenmeyer flask, add 100 cc of limewater (U. S. P.), and shake thoroughly every ten minutes for two hours. Let settle, decant through a filter paper, and collect 50 cc; introduce into a separatory funnel, shake out three times with chloroform, 15 cc each, and then with 15 cc of washed ether.[1] Collect ether-chloroform in another separatory funnel and wash with 10 cc of limewater; return limewater to original solution and reject the immiscible solvent. To the solution now add 20 cc of alcohol, and then enough of a 1 per cent ammonium chlorid solution to free the morphin, testing with wet litmus paper held in the neck of the funnel. Follow with 30 cc of chloroform and shake thoroughly for several minutes. Draw off and shake out with four successive 30 cc portions of a mixture of 5 cc of alcohol and 20 cc of chloroform. Combine the alcohol-chloroform shake-outs and wash with 10 cc of water; pass through a filter wet with chloroform into a tared beaker of 150 cc capacity; evaporate to dryness at a gentle heat, dissolve in 12 cc of fiftieth normal sulphuric acid and titrate back with fiftieth-normal potassium hydroxid, use cochineal as an indicator, and calculate to monohydrate morphin. Multiply the number of cubic centimeters of fiftieth-normal sulphuric acid consumed by 0.006, then by 200 to obtain the weight of crystallized morphin in 100 grams.

There was recovered from U. S. P. tincture of opium camphorated, prepared from the opium sample above referred to, morphin as follows: Each 100 cc contained 4.4 grams of 10.77 per cent (U. S. P. assay). Recovered 0. 0496, 0.0501, and 0.0510 gram of morphin.

For paregoric.—Evaporate 100 cc to 15 cc, wash into separatory funnel, shake out with two portions of washed ether, 15 cc each, and rejecting ether, add 50 cc of limewater; agitate thoroughly, filter and proceed as under opium with the shaking-out process. Titrate the alkaloid as directed above.

For soothing sirups.—Make acid 100 cc of sample and then make slightly alkaline with ammonium-hydroxid, and extract with an alcohol-chloroform mixture to total exhaustion; evaporate on a water or steam bath, take up in 50 cc of limewater, and proceed as under opium.

Morphin habit treatments are usually solutions of morphin sulphate and other alkaloids in water and alcohol. The morphin is generally present in large amounts; when there is present as much as 2 grains per fluid ounce, precipitate the morphin, in the presence of ether with ammonium-hydroxid, filter, wash with alcohol, and then ether, dry, and weigh. Determine morphin in the filtrate by the shake-out process just described and total the two determinations.

The limewater has an advantage over other solvents, as it combines with the morphin and not with the other opium alkaloids, allowing them to be shaken out; also, it leaves a great deal of extraneous matter undissolved. The method avoids a shake out from an acid solution. The other alkaloids are separated and the morphin shaken out in the same preparatory funnel. The time required for a complete determination is less than a seven-hour working day.

PROGRESS IN MICROCHEMICAL TESTS FOR ALKALOIDS.

By B. J. Howard and C. H. Stephenson.

Since the last report on the tests for alkaloids the work has been continued until at present 67 of these compounds have been studied, tests having been made with nearly 40 different reagents, including almost all that have been suggested. As a result about 450 crystalline precipitates have been obtained, of which over 200 have already been photographed to aid in the identification of unknowns as well as for record and publication purposes.

In accord with a previous suggestion, work has been taken up along the line of studying the influence of the presence of a second alkaloid upon the normal reaction

[1] Be sure to remove all uncombined alkaloids at this point; use more solvent if necessary.

for the first. Formerly it was considered probable that a second alkaloid having no reaction with a certain reagent would have no effect upon the positive reaction of that reagent with a given compound. Although this study has been limited, it seems to have already been demonstrated that there are cases where this hypothesis fails. As a result this field of the study becomes more complicated than was at first considered probable.

The reaction between an alkaloid and a given reagent may occur in any one of three ways, namely: (a) As a crystalline precipitate, (b) as a noncrystalline precipitate, either as an amorphous precipitate or as drops of oily material, and (c) as a supersaturated solution. In the second case, it sometimes happens that after being dissolved a crystalline formation takes place spontaneously while in other cases some means must be used to start the change. It also happens that some method must be adopted to start crystallization in the supersaturated condition. The most convenient method which has been used is rubbing the slide with a glass rod. In this connection it is interesting to note that at times it was difficult to start the crystallization even with a rod. After some experimentation it was shown that this often occurred when a glass rod was used which had not been previously employed for this purpose with the particular alkaloidal combination in question. From this observation it is believed that often the active agents are probably minute particles of the product from some previous test, held on the roughened end of the rod, which serve to start the crystallization in other test drops. This fact will be an important one in the practical use of these methods, since failure to produce crystalline forms would lead to erroneous conclusions. It is hoped that some means of avoiding this difficulty may be devised, for although it may not be a serious drawback in the hands of an experienced worker, it would render the methods much less useful for general application.

Although much work still remains to be done before the study will even approach completeness, it is thought that when this is done and an analytical scheme is worked out which at present has only vaguely been attempted, the analytical chemist will find the microchemical tests a valuable aid.

METHODS FOR THE ANALYSIS OF MEDICATED SOFT DRINKS.

By H. C. Fuller.

A study of the composition of soft drinks containing alkaloids and the active principles of drugs was begun in 1907. On investigation it was found that there were no well-defined methods for separating and determining the different ingredients in products of this nature, and it became necessary to work out satisfactory procedures. As a result of this work, several new methods were perfected and are herewith submitted for investigation and criticism.

Methods for the Analysis of Medicated Soft Drinks.

SPECIFIC GRAVITY.

Determine the specific gravity at 20° C. by means of an accurate pyknometer. The figure obtained may be used in subsequent work for calculating the weight of the sample when it is measured out with a standard pipette or flask graduated at 20° C.

TOTAL SOLIDS—VOLATILE CONSTITUENTS—ASH.

Introduce 25 cc of the sample by means of a pipette or flask graduated at 20° C., or weigh an amount equal to that volume, into a 9 cm porcelain (not platinum) evaporating dish, previously tared; dry in a vacuum oven heated at 70° C. for five hours, or evaporate on a steam bath until there is apparently no further loss, then heat for five hours in an oven at 100° to 105° C., cool in a desiccator and weigh rapidly. This weight represents the total solids, and the difference between this figure and the weight of the sample is the volatile matter.

To determine the ash, place the porcelain dish on a triangle, apply a strong flame of a Bunsen burner to the surface of the thick mass. The contents of the dish will gradually intumesce but will not froth over if the flame is not removed or heat applied to the bottom of the dish. When ebullition ceases, cautiously heat the sides of the dish and if no liquid mass exudes through the cracks of the carbonaceous material, gradually bring the flame to the bottom of the dish and heat until the mass is thoroughly charred; cool, thoroughly moisten the char with dilute acetic acid, and place in an oven to dry. When thoroughly dried, heat gradually with a Bunsen flame and finally ignite with a blast flame or in a muffled oven; weigh residue as ash. The operator when igniting the saccharin residue may at first experience some trouble, but with a little care no difficulty should be encountered in carbonizing the entire contents without loss.

ALCOHOL.

The amount of this ingredient is usually small and for this reason samples of from 50 to 100 cc are required to make a determination. Measure this quantity into the distilling apparatus, and rinse the measuring flask with water, using an amount equal to the original volume used. Distil into the flask used for measuring until it is about two-thirds full and fill up to the mark with distilled water. If the liquid is clear and the odor of volatile oils is faint the specific gravity may be determined at once at either 15.6° or 25° C. and the percentage of alcohol by volume obtained from the tables in the Pharmacopœia or U. S. Department of Agriculture, Bureau of Chemistry Bulletin 107, Revised, page 203. Should there be a turbidity or a strong odor of essential oils, the distillate must be further treated according to the following method of Thorpe and Holmes.[1] Transfer to a separator, rinse the flask with a little water, saturate the solution with sodium chlorid, and add 25 cc of petroleum ether, boiling between 40° and 60° C. Shake for five minutes, let stand one-half hour, draw off the lower layer into another separator and shake it out with another portion of petroleum ether. Combine the ethereal extractions, wash them with 25 cc of an aqueous solution saturated with sodium chlorid, draw off the latter, add it to the distillate, and return the resulting mixture to the distillation flask. Distil this mixture to the same volume as was originally employed, determine the specific gravity of the distillate, and calculate the per cent of alcohol as usual.

CAFFEIN.

[When it is desired to determine the caffein in an "extract" or "flavor" proceed as in the method described on p. 192.]

Measure 50 cc of the substance at 20° C., or weigh about this volume into a small beaker, add 5 cc of stronger ammonium hydroxid,[2] allow to digest 12 hours or overnight; then add 2 cc more of strong ammonium hydroxid, heat for two hours; transfer to a large separator, rinsing beaker with water; dilute with about 3 volumes of water, add 5 cc of stronger ammonium hydroxid, and shake out with four successive portions of chloroform, using 50 cc at a time. In case any dyestuff is removed by the chloroform, the combined solutions should be shaken out with a saturated solution of sodium bisulphite, which will remove some of the coloring material.

Collect the chloroform extracts in a flask, recover the bulk of solvent by distillation, then pour the remainder with rinsings into an evaporating dish and evaporate. Dissolve the residue in 25 cc of about 2 per cent sulphuric acid, shake out the acid solution five times with 15 cc portions of chloroform, filter the chloroform solutions into a flask, recover bulk of chloroform and pour remainder of solution with rinsings into a tared dish, evaporate at 100° C., cool, and weigh. If the caffein is not pure, dissolve the residue in 15 cc dilute (10 per cent) hydrochloric acid, add iodin solution (iodin 10 grams and potassium iodid 20 grams dissolved in 100 cc water) in excess, allow the mixture to stand overnight, filter, and wash the precipitate twice with 10 cc of the above iodin solution. Transfer filter paper with precipitate to the original precipitation flask, add sufficient sulphurous acid to dissolve the precipitate with the aid of gentle heat, filter into a separator, wash three times with distilled water, add ammonium hydroxid in excess, shake out four times with 15 cc portions of chloroform, filter the chloroform extracts into a flask, using a small funnel and a 7 cm filter paper and covering with a small watch glass, wash the filter with 5 portions of 5 cc each of chloroform to remove the last portions of caffein; or better, run through absorbent cotton plugged in the stem of the separator. If the final chloroform is colored, concentrate, add a small amount of animal charcoal, rotate several times, and filter. Recover part of the solvent, pour balance into tared dish, evaporate, dry at 100° C., and weigh.

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[1] J. Chem. Soc., 1903, 83: 313.

[2] Containing 28 per cent ammonia.

Pour 200 cc of the product into a large separator, add stronger ammonium hydroxid until alkaline, and shake out with three successive portions of 50 cc each of Prolius mixture (ether 4 parts, chloroform 1 part, alcohol 1 part), collecting the solvent in another separator. If desired, the aqueous solution may be reserved for the detection of salicylic and benzoic acids and saccharin. Filter the combined Prolius extracts into an evaporating dish or beaker, and evaporate over the steam bath, removing the dish as the last traces of the solvent disappear; dissolve the residue in normal sulphuric acid, transfer to a separator, and shake out four times with 15 cc portions of chloroform, collecting the chloroform solutions in another separator. Wash the combined chloroform solutions once with distilled water, discard the chloroform, and add the water to the original acid solution; add 10 cc of petroleum ether boiling at 40° to 50° C., and shake; draw off the acid layer and discard the petroleum ether; add stronger ammonium hydroxid in excess, and shake out three times with 15 cc portions of petroleum ether, collecting the ethereal solutions in another separator. To the latter add 10 cc of distilled water and shake thoroughly; discard the water, and filter the petroleum ether into a beaker; wash filter twice with 10 cc portions of petroleum ether and then evaporate over a steam bath, using a fan. By this method if coca alkaloids are present a nearly colorless residue will be obtained, which will finally crystallize on standing.

The cocain may now be detected by the following reactions; dissolve the residue in petroleum ether and divide into four portions, one of which may be quite small. Evaporate the solvent, and to the small portion add a few drops of normal sulphuric acid; warm gently and filter into a test tube; add a drop of potassium mercuric iodid test solution (Mayer's reagent), and note whether a precipitate is formed. A precipitate would indicate an alkaloid but would not distinguish cocain; if no precipitate occurs it would indicate that no cocain was present and no further tests are necessary.

To another portion add a few drops of concentrated nitric acid and evaporate over the steam bath until the acid is all driven off, then add a few drops of half normal alcoholic potash and note the first odor which comes off. In the presence of cocain a distinct odor of ethyl benzoate will be obtained, but unless one is familiar with the odor a control test should be made.

The residue in the third portion should be applied to the end of the tongue by rubbing with the finger. Cocain will cause a numbness which is not apparent immediately, but develops gradually, and persists for a longer or shorter period, depending on the quantity present. It is advisable to run a parallel experiment with pure cocain in order to become familiar with the physiological effects of this alkaloid.

Remove a portion of the fourth residue and place on a microscopic slide; add a drop or two of a gold chlorid test solution, and stir vigorously with a glass rod, noting the character of the crystals under the microscope. The crystals formed with gold chlorid and cocain are characteristic and should be compared with those obtained with a solution of pure cocain.

The procedure given here for separating the coca alkaloids may be employed if a quantitative estimation is desired. The residue obtained on evaporating the petroleum ether should be weighed and then a titration made as a check on the gravimetric determination. Run in 50 cc of fiftieth-normal sulphuric acid and warm until residue is completely dissolved, then cool and titrate with fiftieth-normal potassium hydrate or sodium hydrate, using cochineal as an indicator. The factor for cocain is 0.006018.

CAFFEIN, COCAIN, AND GLYCERIN IN ONE SAMPLE.

Caffein may be determined quantitatively and cocain and glycerin may be detected by the following method, though the failure to detect cocain should not prevent one from examining further for it, as the alkaloid is liable to be destroyed during the manipulation of the caffein. This method is of no value for estimating glycerin, but will prove reliable if it is desired to simply detect this ingredient.

Measure accurately at 20° C., with a graduated flask or pipette, 50 cc of the sample, or weigh about this volume into an evaporating dish; add 5 cc of stronger ammonium hydroxid, cover dish with watch glass, and allow it to stand 12 hours; add 2 cc more of stronger ammonium hydroxid and evaporate over steam bath until there is no further diminution in volume. Treat the residue with 25 cc portions of 95 per cent alcohol; warm over steam bath; cool, and pour off alcohol into another evaporating dish; repeat this procedure four times and then evaporate the alcoholic extract. Dissolve the residue in 25 cc of approximately 2 per cent sulphuric acid, transfer to separator, shake out 5 times with 15 cc portions of chloroform, running the chloroform extracts into a 250 cc Erlenmeyer flask, and reserve the solution in separator for subsequent testing for cocain and glycerin. Recover part of chloroform, pour rest of solution into an evaporating dish, and evaporate over steam; dissolve the residue in dilute (10 per cent)

hydrochloric acid, transfer to a small flask, add an excess of iodin solution (iodin 10 grams, potassium iodid 20 grams, dissolved in 100 cc of water), rotate the flask; allow precipitate to settle and let stand overnight; filter and wash the flask and precipitate twice with the above iodin solution and then transfer the filter and precipitate to the original precipitation flask; treat with sufficient sulphurous acid to dissolve the precipitate with the aid of gentle heat; filter into a separator, cool, add excess of stronger ammonium hydroxid, shake out four times with 15 cc portions of chloroform; filter extracts into a flask, using a small funnel and a 7 cm filter paper, covered with a watch glass, washing the filter with five portions 5 cc each of chloroform or filter through cotton plugged in the stem of the separator. If the chloroform is still colored decolorize with animal charcoal. Recover part of chloroform and pour the residual solution in the flask into a tared dish; evaporate over steam, dry at not over 100° C., and weigh.

Add an excess of stronger ammonium hydroxid to the original solution from which the caffein was removed; shake out three times with petroleum ether, boiling at 40° to 60° C., filtering ether extractions into four small beakers; evaporate solvent and examine residues for cocain, as described in the preceding method.

Evaporate the solution remaining in the separator after shaking out the caffein and cocain with milk of lime. Continue as directed in Bulletin No. 107, Revised, page 83, "Glycerol in Wines." This method can be depended upon for approximate results.

SUGAR DETERMINATIONS.

Use the Munson-Walker methods described in Bulletin 107, Revised, pages 40 and 42.

PHOSPHORIC ACID.

Measure 25 cc of the sample with a flask or pipette graduated at 20° C. or weigh an amount equal to this volume into a 250 cc beaker, heat until alcohol is all driven off; dilute with water to about 100 cc and add 30 cc of stronger ammonium hydroxid. Run in slowly from a burette 50 cc of magnesia mixture, U. S. P. test solution, stirring vigorously; allow precipitate to settle; run in 1 or 2 cc more of magnesia mixture, to see whether precipitation is complete; add 25 cc of stronger ammonium hydroxid and let stand overnight.

Filter and wash precipitate three times with 2 per cent of ammonium hydroxid; dissolve in 15 cc of 10 per cent nitric acid, washing filter three times with distilled water; add excess of ammonium molybdate, U. S. P. test solution, and heat to 50° C.; filter and wash precipitate with distilled water until free of acid. The precipitate may be treated in either of two ways; it may be transferred to a beaker with distilled water, dissolved in excess of standard potassium hydrate solution, 1 cc of which equals 0.0010 gram of phosphoric acid (P_2O_5), and the excess titrated with standard hydrochloric acid of the same strength (Bulletin 107, Revised, Bureau of Chemistry), or the precipitate may be dissolved in 10 to 20 cc of stronger ammonium hydroxid and the filter washed three times with boiling water, the mixture cooled, and magnesia mixture added drop by drop with vigorous stirring, 25 cc stronger ammonium hydroxid added, and the mixture allowed to stand overnight. Filter into an ashless filter paper, wash three times with 1 per cent ammonium hydroxid, dry, ignite and weigh as magnesium pyro-phosphate ($Mg_2P_2O_7$); if the precipitate does not burn white, cool, add a few drops of concentrated nitric acid, evaporate dry and again ignite. Calculate the phosphoric acid (P_2O_5), from the weight of magnesium pyro-phosphate ($Mg_2P_2O_7$).

SALICYLIC AND BENZOIC ACIDS AND SACCHARIN.

To detect the presence of these ingredients the ammoniacal solution from which the cocain was extracted may be employed, or if desired a fresh sample may be used. Add an excess of dilute 10 per cent sulphuric acid, shake out three times with 50 cc portions of Prolius's mixture; combine the extracts, filter into a beaker, and evaporate over a steam bath, using fan.

The presence of appreciable quantities of saccharin in the residue is readily detected by the sweet taste. This may be confirmed by heating with sodium hydrate in a test tube to 215° C. in an oil bath and finally detecting the salicylic acid formed (Bulletin 107, Revised, Bureau of Chemistry, p. 182).

If salicylic acid is present in the residue a small portion on warming with water and subsequent cooling will give the characteristic purple color with solution of ferric chlorid. If both salicylic acid and saccharin are present the former must be removed before fusing the saccharin with sodium hydrate. Dissolve the residue in dilute hydrochloric acid, add bromin water in excess, shake well and filter; salicylic acid

is completely removed as the bromin derivative; make the filtrate strongly alkaline with sodium hydrate test solution, evaporate, heat to 215° C., and finally extract the salicylic acid formed.

Benzoic acid in the residue may be detected by placing the beaker covered with a watch glass on the top of a steam or water bath, but not exposed to the steam; the acid will soon form a sublimate on the watch glass and the cool portion of the beaker, and may be confirmed by its melting point. If salicylic acid occurs with benzoic it may be removed by bromin water as described above. The solution after filtering should be rendered alkaline and then slightly acidified and the benzoic acid shaken out with ether.

DYESTUFFS.

For the detection and determintaion of added coloring matters use the methods described in Bulletin 107, Revised, Bureau of Chemistry, page 190.

ANALYSIS OF BEEF, IRON, AND WINE.

By E. A. Ruddiman and L. F. Kebler.

This study was made for the purpose of ascertaining, first, the best method for determining the amount of extract of beef represented by the preparation "beef, iron, and wine," particularly in the presence of iron and ammonium citrate; second, for determining the average percentage of alcohol present, and, third, to establish the characteristics which should distinguish the National Formulary preparation. Five representative commercial extracts of beef were purchased in the open market and the percentage of total nitrogen in each was estimated by the Gunning method with the following results: (a) 7.615 per cent; (b) 9.28 per cent; (c) 4.242 per cent; (d) 6.707 per cent; (e) 6.654 per cent.

The difficulty of estimating the nitrogen of ammonium compounds in the presence of extract of beef is due to the fact that the extract contains compounds which are easily decomposed, forming other compounds that act like ammonia. The following are some of the methods tried for the separation of ammonium nitrogen and beef extract nitrogen.

Mixtures of extract of beef, water, and iron and ammonium citrate were made. Attempts were then made to liberate the ammonia from the ammonium salt by the addition of such compounds as magnesium oxid, barium carbonate, calcium carbonate, calcium phosphate, and zinc oxid, distilling off the ammonia at the ordinary pressure, and under diminished pressure. Any method that would liberate all of the ammonia from the double salt also appeared to decompose some of the nitrogenous compounds of the beef, with the formation of compounds which act like ammonia.

An attempt was next made to effect separation by precipitating the albuminous matter by tannic acid and alum, filtering, and precipitating the easily decomposed beef compounds by the addition of phosphotungstic acid, leaving the ammonium compound in solution, but it was found that the ammonium compound was also precipitated. Oxidizing agents were added with the hope of decomposing the beef compounds which are so easily changed into compounds resembling ammonia, but without success.

Another plan proposed for determining the nitrogen which comes from the ammonia when iron and ammonium citrate is used in making beef, iron and wine was to estimate the amount of iron and from that calculate the amount of nitrogen that would come from the double compound. Samples of iron and ammonium citrate vary in composition and to determine whether the proportion of nitrogen to iron is sufficiently constant several samples of this double salt were purchased and analyzed with the results shown in the following table:

Commercial samples of iron and ammonium citrate.

Description and number of sample.	Nitrogen. (A)	Iron (U. S. P. method). (B)	Total iron. (C)	Amount of nitrogen to 1 gram of iron (U. S. P. method). (D)	Amount of nitrogen to 1 gram of total iron. (E)
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
2261a	6.750	17.594	17.748	0.383	0.380
2262a	6.260	22.546	22.813	.277	.274
2263a	6.228	22.562	22.688	.276	.274
2264a	5.995	20.061	20.149	.298	.297
2265a	6.284	21.672	21.749	.289	.288
2266a	6.331	21.866	21.863	.289	.289
2267a	6.617	17.149	17.235	.385	.383
2268a	5.034	19.330	19.664	.260	.256
2269a	6.076	21.899	21.920	.277	.277
2270a	6.802	17.169	17.294	.396	.393
2271a	6.312	21.853	21.984	.288	.287
1575	5.733	19.300	19.789	.291	.284
1576	4.717	18.386	18.511	.256	.254
1577	6.273	22.256	22.242	.281	.282
Average	6.100	20.260	20.403	.303	.301

The nitrogen was calculated from the ammonia liberated by barium carbonate. Column B gives the per cent of iron obtained by using the U. S. P. method which estimates the iron in the ferric condition only, not the ferrous. Column C gives the total percentage of iron and shows that there is generally some ferrous iron in this compound. Column D shows the amount of nitrogen for 1 gram of iron obtained by the U. S. P. method and Column E the same except for 1 gram of total iron. The organic matter was destroyed by means of a little sulphuric acid and heat. The approximate amount of nitrogen from the ammonium salt can be obtained by multiplying the weight of metallic iron by the factor 0.3, but any additional ammonium salt that might be used would be estimated as beef.

Finally it was decided to determine the total amount of nitrogen in 50 cc of beef, iron, and wine by the Gunning method and to determine the amount of nitrogen in the compounds which act like ammonia and which are formed by the action of barium carbonate on the beef extract in 50 cc of the preparation. In case of a preparation in which iron and ammonium citrate is used instead of the tincture of the citro-chlorid of iron, the excess of nitrogen from the ammoniacal compounds liberated by barium carbonate over the nitrogen of the beef is to be considered as coming from the iron and ammonium citrate and should be deducted from the total nitrogen of the preparation to get the nitrogen due to the beef extract. Several preparations of beef, iron, and wine were made as directed by the National Formulary, using the beef extracts previously mentioned. The results are given in the accompanying table.

Examination of commercial samples bought on the market and samples made up according to the National Formulary, using commercial beef extracts.

Samples.	Total nitrogen in 50 cc (Gunning method).	Nitrogen in 50 cc (barium carbonate method).	Iron found in 50 cc.	Amount of iron salt claimed in each fluid ounce.	Alcohol obtained.	Alcohol claimed.	Specific gravity at 25° C.
Commercial samples:	*Grams.*	*Grams.*	*Grams.*	*Grains and minims.*	*Per cent.*	*Per cent.*	
1	0.1227	0.0060	0.0704	16 m Tr. citro-chlorid	17.0	18.0	1.0502
2	.0799	.0030	.0238	2 gr soluble salt of iron.	18.3	24.0	1.0341
3	.0651	.0028	.0549	4 gr citrate of iron	22.0	Not more than 20 per ct.	1.0455
4	.0760	.0183	.0421	2 gr soluble cit. of iron.	19.5	20.0	1.0369
5	.0746	.0043	.0627	16 m Tr. citro-chlorid.	15.2	20.0	1.0322
6	.0818	.0055	.0602	do	19.8	25.0	1.0386
7	.0601	.0184	.0455	2 gr iron and ammon. citrate.	19.3	17.5	1.0204
8	.1496	.0274	.0765	4 gr iron and ammon. citrate.	23.0	25.0	1.0372
Made according to National Formulary:							
9. Extract A (Mar.).[1]	.1124	.0042	.0807		15.6		1.0503
10. Extract A (Sept.).	.1078	.0040			16.5		
11. Extract B (Mar.).	.1465	.0048	.0799		15.9		1.0509
12. Extract B (Sept.).	.1359	.0046			16.5		
13. Extract B (iron left out).	.1462	.0016			15.5		
14. Extract C (Mar.).	.0700	.0046	.0818		15.5		1.0555
15. Extract C (iron left out).	.0684	.0022			15.5		
16. Extract C (Sept.).	.0663	.0044			16.5		
17. Extract D (Mar.).	.1179	.0073	.0800		14.4		1.0751
18. Extract D (Sept.).	.0901	.0051			16.7		
19. Extract D (Oct.).	.0918	.0063			16.5		
20. Extract E (Mar.).	.1281	.0055	.0796		14.3		1.0749
21. Extract E (Sept.).	.0921	.0042			16.2		
22. Extract E (Oct.).	.0908	.0048					

[1] The samples made in March were analyzed a few days after they were finished; those made in September stood about a month, and those made in October over a year, before being examined. (See p. 195 for nitrogen content of commercial samples A to E, used in making up these samples.)

On inspecting the amounts of total nitrogen obtained from the National Formulary preparations it will be seen that the amount of nitrogen in 50 cc falls below 0.09 gram only in the case of one extract, which was previously shown to be low in nitrogen. If a good beef extract [1] is used the total nitrogen should not be below 0.10 gram in 50 cc of the preparation. In order to determine whether this preparation loses much

[1] A good beef extract has been defined by the joint committee of the Association of State and National Food and Dairy Departments and the Association of Official Agricultural Chemists as follows: "Meat extract is the product obtained by extracting fresh meat with boiling water and concentrating the liquid portion by evaporation after the removal of fat, and contains not less than 75 per cent of total solids, of which not over 27 per cent is ash and not over 12 per cent is sodium chlorid (calculated from the total chlorin present), not over 0.6 per cent is fat, and not less than 8 per cent is nitrogen. The nitrogenous compounds contain not less than 40 per cent of meat bases and not less than 10 per cent of kreatin and kreatinin."

nitrogen by precipitation on long standing, Sample 2 was reestimated after about twenty months, obtaining 0.0787 gram, a loss of 0.0012 gram. Sample 5 lost 0.0010 gram; Sample 14 gained 0.0002 gram; Sample 17 gained 0.0021 gram; Sample 10 gained 0.0007 gram; Sample 16 lost 0.0020 gram; and Sample 18 gained 0.0003 gram. Of the eight samples purchased only two come up to the proposed standard of 0.10 gram of total nitrogen for 50 cc.

The figures showing the nitrogen liberated by barium carbonate from 50 cc of the National Formulary preparations show that in only two cases was the amount over 0.006 gram.

The percentage of alcohol is liable to vary considerably, depending upon the degree of evaporation practiced by the manufacturer and the alcoholic strength of the wine.

Theoretically the amount of iron in 50 cc should be about 0.0736 gram calculated as metallic iron; a limit of from 0.07 to 0.08 gram is suggested.

It would appear in the light of the results here reported that a beef, iron, and wine made according to the National Formulary should possess the following characteristics:

Fifty cubic centimeters of beef, iron, and wine when assayed by the Gunning process for total nitrogen should yield not less than 0.10 gram of nitrogen coming from the beef extract. If the amount of nitrogen obtained by the barium carbonate method exceeds 0.006 gram, the excess is to be considered as coming from an ammonium compound and is to be deducted from the total nitrogen obtained, the remainder representing the nitrogen coming from the beef extract. Fifty cubic centimeters should contain not less than 0.07 gram nor more than 0.08 gram of iron calculated as metallic iron. The percentage of alcohol should not be under 14 nor over 20.

METHODS OF ANALYSIS.

To determine the total nitrogen: Introduce 50 cc of beef, iron, and wine into a 500 cc Kjeldahl flask. Add about 5 drops of concentrated sulphuric acid and evaporate to a solid on a water bath, preferably evaporating under diminished pressure. To the residue add 10 grams of potassium sulphate and 50 cc of concentrated sulphuric acid. Heat slowly at first, increasing the heat as the frothing ceases and digest until the liquid becomes colorless or nearly so. After cooling add 200 cc of water, a few drops of phenolphthalein solution, and 60 cc of a saturated solution of sodium hydroxid, or a sufficient amount to make the mixture strongly alkaline, pouring down the side of the flask so that it will not mix with the acid. Add a few pieces of granulated zinc or pumice stone to keep the liquid from bumping. Connect the flask by means of a bulb tube with an upright spiral condenser. Distil, catching the distillate in 110 cc of decinormal sulphuric acid, until from 150 cc to 200 cc of distillate has been received. Titrate back the excess of acid with decinormal sodium hydroxid. Subtract the number of cubic centimeters of alkali used from the number of cubic centimeters of acid used and multiply the remainder by 0.001393; the product will be the weight of total nitrogen.

To determine the nitrogen in the ammonia liberated by barium carbonate: Introduce 50 cc of beef, iron, and wine into a 500 cc Kjeldahl flask, add 200 cc of water, 3 grams of barium carbonate, and a few pieces of granulated zinc or pumice stone. Connect the flask with the condenser as in the preceding method. Distil until the residue measures about 50 cc, catching the distillate in 25 cc of decinormal sulphuric acid. Titrate back the excess of acid with decinormal sodium hydroxid. Subtract the number of cubic centimeters of alkali used from that of the acid and multiply the remainder by 0.001393; the product will be the amount of nitrogen.

The alcohol and iron are to be estimated by the usual methods.

The association adjourned.

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Determination of nitrogen: F. Thompson, Newark, Del.
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Vegetable proteids: R. Harcourt, Guelph, Canada.
Potash:
Determination: T. Bragg, Auburn, Ala.
Availability: H. H. Hill, Blacksburg, Va.
Soils: G. S. Fraps, College Station, Tex.
Dairy products: E. M. Bailey, New Haven, Conn.
Foods and feeding stuffs: E. V. McCollum, Madison, Wis.
Food adulteration:
Colors: W. E. Mathewson, New York City.
Saccharine products: S. H. Ross, Omaha, Nebr.
Fruit products: A. W. Blair, Gainesville, Fla.
Wine: E. J. Lea, Berkeley, Cal.
Beer: W. D. McAbee, Indianapolis, Ind.

Food adulteration—Continued.
Distilled liquors: J. O. LaBach, Lexington, Ky.
Vinegar: W. A. Bender, New York City.
Flavoring extracts: R. S. Hiltner, Denver, Colo.
Spices, R. W. Hilts, Philadelphia, Pa.
Baking powder: E. W. Magruder, Richmond, Va.
Meat and fish: Ralph Hoagland, St. Anthony Park, St. Paul, Minn.
Fats and oils: H. S. Bailey, Washington, D. C.
Dairy products: A. E. Paul, Chicago, Ill.
Cereal products: H. L. White, Agricultural College, N. D.
Vegetables: J. P. Street, New Haven, Conn.
Condiments other than spices: W. J. McGee, New Orleans, La.
Cocoa and cocoa products: W. L. Dubois, Buffalo, N. Y.
Tea and coffee: M. E. Jaffa, Berkeley, Cal.
Preservatives: H. E. Barnard, Indianapolis, Ind.
Water in foods: H. C. Lythgoe, Boston, Mass.
Organic and inorganic phosphorus in foods: H. S. Grindley, Urbana, Ill.
Sugar: C. S. Hudson, Washington, D. C.
Insecticides: S. D. Averitt, Lexington, Ky.
Medicinal plants and drugs:
Medicinal plants—
Albert Schneider, San Francisco, Cal.
H. H. Rusby, New York City.
Synthetic products: W. O. Emery, Washington, D. C.
Medicated soft drinks: H. C. Fuller, Washington, D. C.
Water: C. E. Bradley, Corvallis, Oreg.
Tannin: Burton Ray, West Raleigh, N. C.
Inorganic plant constituents: W. H. McIntire, State College, Pa.

SPECIAL COMMITTEES.

Amendments to the Constitution.

L. L. Van Slyke, Geneva, N. Y., chairman.
B. B. Ross, Auburn, Ala.
William Frear, State College, Pa.

Appropriation.

John Phillips Street, New Haven, Conn., chairman.
R. J. Davidson, Blacksburg, Va.
H. E. Barnard, Indianapolis, Ind.

Availability of Phosphoric Acid in Basic Slag.

W. F. Hand, Agricultural College, Miss., chairman.
C. B. Williams, West Raleigh, N. C.
C. G. Hopkins, Urbana, Ill.
H. D. Haskins, Amherst, Mass.
John S. Burd, Berkeley, Cal.

Cooperation with Other Agricultural Organizations.

[At request of Society for the Promotion of Agricultural Science.]

H. W. Wiley, Washington, D. C., chairman.
W. D. Bigelow, Washington, D. C.
F. W. Woll, Madison, Wis. (alternate, C. B. Williams, West Raleigh, N. C.).

Food Standards.

William Frear, State College, Pa., chairman.
H. W. Wiley, Washington, D. C.
H. A. Weber, Columbus, Ohio.
M. A. Scovell, Lexington, Ky.
E. H. Jenkins, New Haven, Conn.

Journal of Agricultural Research.

W. A. Withers, Raleigh, N. C., chairman.
H. W. Wiley, Washington, D. C.
C. G. Hopkins, Urbana, Ill.
M. E. Jaffa, Berkeley, Cal.
A. M. Peter, Lexington, Ky.

Participation in the Eighth International Congress of Applied Chemistry.

J. P. Street, New Haven, Conn., chairman.
F. K. Cameron, Washington, D. C.
R. Harcourt, Guelph, Canada.
J. G. Lipman, New Brunswick, N. J.
R. W. Thatcher, Pullman, Wash.

Presentation of the Question of Unification of Terms to the International Congress of Applied Chemistry.

R. J. Davidson, Blacksburg, Va., chairman.
C. G. Hopkins, Urbana, Ill.
W. D. Bigelow, Washington, D. C.
G. S. Fraps, College Station, Tex.
B. W. Kilgore, Raleigh, N. C.
H. J. Wheeler, Kingston, R. I.
J. T. Willard, Manhattan, Kans.

Recommendation of Referees and Revision of Methods.

[Figures in parentheses refer to year in which appointment expires.]

A. L. Winton, chairman.

Subcommittee A: W. W. Skinner (1916), B. B. Ross (1914), *J. P. Street (1912), chairman, Agricultural Experiment Station, New Haven, Conn.*

Subcommittee B: H. E. Barnard (1916), *E. M. Chace (1914), chairman, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.*, J. M. Bartlett (1912).

Subcommittee C: P. F. Trowbridge (1916), C. D. Howard (1914), *A. L. Winton (1912), chairman, U. S. Food and Drug Inspection Laboratory, Chicago, Ill.*

Standardization of Alcohol Tables.

L. M. Tolman, Washington, D. C., chairman.
M. E. Jaffa, Berkeley, Cal.
A. B. Adams, Washington, D. C.
R. J. Davidson, Blacksburg, Va.
H. E. Barnard, Indianapolis, Ind.

Testing of Chemical Reagents.

L. F. Kebler, Washington, D. C., chairman.
A. L. Winton, Chicago, Ill.
B. W. Kilgore, Raleigh, N. C.

Unification of Methods of Analysis of Fats and Oils.

L. M. Tolman, Washington, D. C., chairman.
P. H. Walker, Washington, D. C.
A. Lowenstein, Chicago, Ill.

CONSTITUTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

(1) This association shall be known as the Association of Official Agricultural Chemists of North America. The objects of the association shall be (1) to secure uniformity and accuracy in the methods, results, and modes of statement of analysis of fertilizers, soils, cattle food, dairy products, human foods, medicinal plants, drugs, and other materials connected with agricultural industry; (2) to afford opportunity for the discussion of matters of interest to agricultural chemists.

(2) Analytical chemists connected with the United States Department of Agriculture, or with any State, provincial, or national agricultural experiment station or agricultural college, or with any State, provincial, or national institution or body in North America charged with official control of the materials named in section 1, shall alone be eligible to membership; and one such representative for each of these institutions or boards, when properly accredited, shall be entitled to enter motions or vote in the association. Only such chemists as are connected with institutions exercising official fertilizer control shall vote on questions involving methods of analyzing fertilizers, or involving definitions, nomenclature, laws, or regulations relating to fertilizers. Only such chemists as are connected with institutions exercising official cattle-food control shall vote on questions involving methods of analyzing cattle foods or involving nomenclature, definitions, laws, or regulations relating to cattle foods. Only such chemists as are connected with institutions exercising official food or drug control shall vote on questions involving methods of analyzing food or drugs, or involving nomenclature, definitions, laws, or regulations relating to food or drugs. All persons eligible to membership shall become members ex officio and shall be allowed the privileges of membership at any meeting of the association after presenting proper credentials. All members of the association who lose their right to such membership by retiring from positions indicated as requisite for membership shall be entitled to become honorary members and to have all privileges of membership save the right to hold office and vote. All analytical chemists and others interested in the objects of the association may attend its meetings and take part in its discussions, but shall not be entitled to enter motions or vote.

(3) The officers of the association shall consist of a president, a vice president, and a secretary, who shall also act as treasurer; and these officers, together with two other members to be elected by the association, shall constitute the executive committee. When any officer ceases to be a member by reason of withdrawing from a department or board whose members are eligible to membership, his office shall be considered vacant, and a successor may be appointed by the executive committee, to continue in office till the annual meeting next following.

(4) There shall be appointed by the executive committee, at the regular annual meeting, from among the members of the association, a referee and such associate referees for each of the subjects to be considered by the association as that committee may deem appropriate.

It shall be the duty of these referees to prepare and distribute samples and standard reagents to members of the association and others desiring the same, to furnish blanks for tabulating analyses, and to present at the annual meeting the results of work done, discussion thereof, and recommendations of methods to be followed.

(5) The special duties of the officers of the association shall be further defined, when necessary, by the executive committee.

(6) The annual meeting of this association shall be held at such place as shall be decided by the association, and at such time as shall be decided by the executive committee, and announced at least three months before the time of meeting.

(7) No changes shall be made in the methods of analysis used in official inspection, except by unanimous consent, until an opportunity shall have been given all official chemists having charge of the particular inspection affected to test the proposed changes.

(8) Special meetings shall be called by the executive committee when in its judgment it shall be necessary, or on the written request of five members; and at any

meeting, regular or special, seven enrolled members entitled to vote shall constitute a quorum for the transaction of business.

(9) The executive committee will confer with the official boards represented with reference to the payment of expenses connected with the meetings and publication of the proceedings of the association.

(10) All proposed alterations or amendments to this constitution shall be referred to a select committee of three at a regular meeting, and after report from such committee may be adopted by the approval of two-thirds of the members present entitled to vote.

By-Laws.

(1) Any amendment to these by-laws or addition thereto may be proposed at a meeting of the association and shall then be published in the Proceedings. It may then be adopted by a majority vote of the association at the next meeting.

(2) These by-laws or any portion of them may be suspended without previous notice by a unanimous vote of those present at any meeting of the association.

(3) There shall be a committee of nine members which shall be designated as the committee on recommendations of referees. The president shall appoint three members of this committee to serve six years, such appointments to be made every other year as the terms expire. The chairman of the committee shall be appointed by the president and shall divide the nine members into three subcommittees (A, B, and, C), and shall assign to each subcommittee the reports and subjects it shall consider.

(4) Each referee shall forward to the chairman of the committee on recommendations at least three weeks before the meeting of the association his recommendations and a sufficient abstract of his report to enable the committee to act intelligently on the recommendations.

(5) A method shall not be adopted as provisional or a provisional method amended until such method or amendment has been reported by the appropriate referee and published in the Proceedings of the association.

(6) A method shall not be adopted as official or an official method amended until such method or amendment has been recommended as official for at least two years by the appropriate referee.

(7) Each college, experiment station, bureau, board, or other institution entitled to representation in the association shall contribute annually $2, and its representatives shall not be qualified to vote or hold office in the association unless such annual dues have been paid, but these shall not be cumulative.

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